

Comparison of Conducting Polymer Actuators Based on Polypyrrole Doped with BF₄⁻, PF₆⁻, CF₃SO₃⁻, and ClO₄⁻

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Polypyrrole films prepared from aromatic ester solutions of tetrabutylammonium tetrafluoroborate (TBABF₄), tetrabutylammonium hexafluorophosphate (TBAPF₆), tetrabutylammonium trifluoromethanesulfonate (TBACF₃SO₃), and tetrabutylammonium perchlorate (TBAClO₄) exhibited large electrochemical strain (11.2–14.0%) and stress (10.6–22.0 MPa) when cycled between -0.9 V and +0.7 V vs Ag/Ag⁺ at 2 mV s⁻¹ and 10 mV s⁻¹, respectively, in an aqueous NaPF₆ solution, amongst which PPy-CF₃SO₃⁻ solely elongated mechanically by 60–100%. It is therefore more suitable for practical artificial muscle devices. Although polypyrrole actuators doped with ClO₄⁻ exhibited moderate strains for a decade, a PPy-ClO₄⁻ actuator prepared from an aromatic ester solution has showed large electrochemical strain (11.2–13.5%) and stress (12.3–15.2 MPa). When cycled at 100 mV s⁻¹, polypyrrole actuators exhibited approximately twice as large electrochemical stress as those measured at 10 mV s⁻¹, because the PPy strip was kept in the doped state (the weakest state) for a shorter time, and early breakage did not occur to give a larger electrochemical stress. Polypyrrole actuators might not be very stable when showing the maximum performance, but the electrochemical strain remained almost constant up to 100 cycles under moderate conditions, such as being driven at 0.1 Hz.

Conducting polymers (CPs), such as polypyrrole (PPy), polythiophene, and polyaniline, expand and contract with doping and dedoping, respectively, driven electrochemically, and exhibit a large electrochemical stress (3–5 MPa), ^{1–4} 10-times larger than that (0.35 MPa)⁵ of skeletal muscles. The large electrochemical stress has been attracting researchers and engineers, who expect that CP actuators can be used as artificial muscles. The electrochemical stress of CP actuators is certainly much larger than that (0.3 MPa)^{5,6} of ionic polymer gels, another candidate for a polymeric actuator. The moderate electrochemical strain $(1-3\%)^{2,3}$ of CP actuators has been an obstacle to the practical use of CP actuators as artificial muscles. Bay et al. reported that a PPy doped with dodecyl benzenesulfonate (DBS) having a gold compliant electrode exhibited 12% electrochemical strain when cycled between +0.2 V and -0.9V vs saturated calomel electrode at 2 mV s⁻¹ in an aqueous NaCl solution. The gold compliant electrode significantly improved the electrochemical strain because the DBS-doped PPy without the gold electrode showed only 5.6% and 2.5% strain with and without the addition of 1-pentanol as a co-surfactant, respectively, in the preparation of DBS-doped PPy.8

Recently, we have reported that PPy films, prepared from a methyl benzoate solution of $TBABF_4$ on a Ti electrode, exhibited 12.4% electrochemical strain. This PPy film doped with BF_4^- was the first CP actuator showing more than 10% strain without any additional electrode. The BF_4^- -doped PPy actuator exhibited 22 MPa stress with 1% strain, and 5 MPa with 7%, and was therefore considered to be the first practical CP actuator. Soon after the breakthrough, we found a PPy film, prepared similarly with $TBACF_3SO_3$ as the electrolyte, to ex-

hibit not only a similar maximum electrochemical strain (12.8%) and stress (20.8 MPa) to those of the PPy doped with BF₄⁻, but also good flexibility and mechanical elongation up to 100%. 11 The flexible and tough CF₃SO₃-doped PPy film has therefore been mainly used for fabricating CP actuator devices. 10,12 Novel CP actuators based on PPy should be applicable to robots, powered suits, artificial limbs, control devices, switches, toys, gadgets, medical devices, etc. These applications cannot be realized without collaboration with researchers and engineers from a variety of disciplines. Further, actuator materials that are easy to handle for fabricating devices should be developed. A tailor-made actuator comprising PPy-metal coil composite^{13,14} should be one of the actuator materials used to fabricate practical devices. Stretchable framework supported CP actuators, like the PPy-metal coil composite, have enhanced the use of the CP actuators.

As Smela pointed out,¹⁵ there are too many factors to map out the relationships between the preparation, material properties, and metrics. Moreover, researchers on CP actuators have been using different materials under different conditions to investigate CP actuators, resulting in some difficulty in interpreting the literature. Finally, she recommended that two commonly studied PPy actuators, such as PPy doped with ClO₄⁻ prepared from acetonitrile with 2% water and PPy doped with DBS, should be used in order to understand how to systematically control for device behavior. According to our results, however, neither of the two recommended PPy actuators showed a large electrochemical strain, and therefore we believe "practical" CP actuators with a large strain and stress should be studied first.

We describe in this paper the actuator performance of PPy films prepared with TBABF₄, TBAPF₆, TBACF₃SO₃, and TBAClO₄ as the electrolyte. All of these have exhibited more than 10% electrochemical strain under appropriate conditions of electropolymerization and electrochemical stretching. In order to discuss the actuation mechanisms, the electrochemical stretching and properties of PPy films doped with BF₄ $^-$, PF₆ $^-$, CF₃SO₃ $^-$, and ClO₄ $^-$ were studied.

Experimental

Materials. Pyrrole (Wako Pure Chemical Industries, Ltd.), methyl benzoate (Wako), ethyl benzoate (Wako), butyl benzoate (Wako), *t*-butyl acetate (Wako), dimethyl phthalate (Wako), diethyl phthalate (Wako), 1,2-dimethoxyethane (Wako), 1,4-butanediol (Wako), 4-methyl-1,3-dioxolan-2-one (propylene carbonate, PC) (Wako), tetrabutylammonium tetrafluoroborate (TBABF₄) (Aldrich), tetrabutylammonium hexafluorophosphate (TBAPF₆) (Tokyo Kasei Kogyo Co., Ltd.), tetrabutylammonium trifluoromethanesulfonate (TBACF₃SO₃) (Lancaster Synthesis, Inc.), tetrabutylammonium perchlorate (TBAClO₄) (Tokyo Kasei), sodium hexafluorophosphate (NaPF₆) (Sigma-Aldrich, Inc.), sodium tetrafluoroborate (NaBF₄) (Wako), and sodium chloride (Wako) were purchased and used without further purification.

Preparation of PPy Films. The preparation of PPy films was performed by a current-constant electropolymerization (0.2 mA cm $^{-2}$) of pyrrole (0.25 mol dm $^{-3}$) using a two-electrode one-compartment cell typically from a methyl benzoate solution of TBACF₃SO₃ (0.2 mol dm $^{-3}$) at 0 °C for 4 h on a Ti, Pt, or ITO electrode, driven by a Hokuto Denko HA-151 potentiostat–galvanostat. Obtained PPy films (typically 10 cm 2 , 80 cm 2 , and 200 cm 2) were immersed in acetone, peeled off from the electrode, and air-dried.

Measurements of PPy Films. A cyclic voltammogram (CV) and an electrochemomechanical deformation (ECMD) of freestanding PPy films were typically measured in an aqueous NaPF₆ solution (1.0 mol dm⁻³) at room temperature, cycled between -0.9 V and +0.7 V vs Ag/Ag⁺ at 2 mV s⁻¹, with a Princeton Applied Research 263A potentiostat-galvanostat. 10,16 Electrochemical contraction of PPy films was carried out by applying -0.7V vs Ag/Ag⁺ at room temperature in an aqueous NaPF₆ solution. A PPv strip (typically 15-mm length × 2-mm width, thickness: ca. 20 µm) was put in a three-electrode cell using a Pt plate and a PTFE holder, and used as the working electrode. A Pt plate and an Ag wire were used as the counter electrode and the reference electrode, respectively. The change in length (Δl) of the strip was monitored by a KEYENCE LE-4000 laser displacement meter. The definition of the electrochemical strain (%) of the PPy strip was $(\Delta l/l_0) \times 100$, where l_0 was the original length of the PPy strip.

To evaluate the maximum stress induced electrically of PPy actuators, two different procedures were applied. One has already been described elsewhere, 10,11 and possibly underestimated the maximum stress. The maximum electrochemical stress was measured by increasing the load until the PPy strip was broken (breaking stress), when cycled between -0.9~V and $+0.7~V~vs~Ag/Ag^+$ at $10~mV~s^{-1}$. Another method was to sweep at $100~mV~s^{-1}$ in order not to severely damage the PPy strip.

Measurements of the electric conductivity, thickness, surface morphology, and mechanical properties of PPy films have been described elsewhere. 10,11

Results and Discussion

Electrochemomechanical Stretching of PPy Films Doped with Various Anions. Figures 1–4 illustrate the CVs and ECMDs of PPy films prepared from a methyl benzoate solution of TBABF4, TBAPF6, TBACF3SO3, or TBAClO4, respectively, as the electrolyte, and driven similarly in aqueous NaPF6 solution (1.0 mol dm $^{-3}$) between -0.9 V and +0.7 V vs Ag/Ag $^+$ at 2 mV s $^{-1}$. The CV and the ECMD of PPy doped with PF6 $^-$ driven in an aqueous NaPF6 solution (shown in Fig. 2) were quite similar to those of PPy doped with BF4 $^-$ (Fig. 1). The difference was, roughly speaking, the dopant anion size used for the electropolymerization of pyrrole. As mentioned elsewhere, 9,10 the electrochemical strain of the BF4 $^-$ -doped PPy strongly depended on the anion size of the electrolyte used to measure the electrochemical stretching, as follows:

$$PF_6^- > BF_4^- > Cl^-.$$
 (1)

In this work, aqueous NaPF $_6$ was employed for the electrochemical stretching of the BF $_4$ ⁻- or the PF $_6$ ⁻-doped PPy, and the electrochemical strain was found to be almost the same, as indicated in Table 1. Consequently, the electrochemical strain of PPy actuators was found not to depend on the anion used for electropolymerization, but on the anion used for electrochemical stretching as long as reversible dopant insertion and expulsion occurred.

Compared with BF_4^- and PF_6^- doped PPy, $CF_3SO_3^-$ doped PPy is somewhat different. Not only is the ionic radius of $CF_3SO_3^-$ (0.270 nm)¹⁷ bigger than those of BF_4^- (0.229

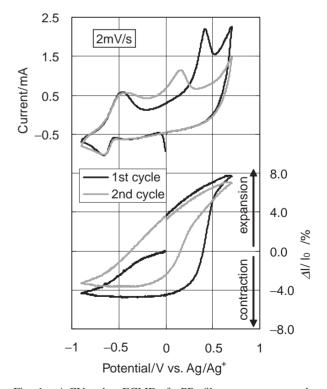


Fig. 1. A CV and an ECMD of a PPy film actuator prepared from a methyl benzoate solution of TBABF₄ on a Ti electrode, cycled between -0.9~V and +0.7~V at 2 $mV\,s^{-1}$ in aqueous NaPF₆ solution.

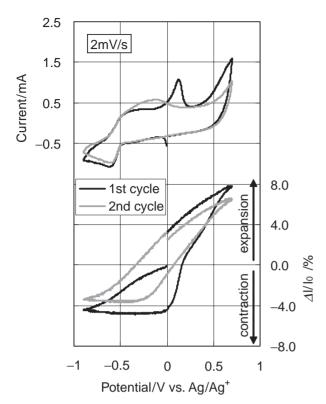


Fig. 2. A CV and an ECMD of a PPy film actuator prepared from a methyl benzoate solution of TBAPF₆ on a Ti electrode, cycled between -0.9 V and +0.7 V at 2 mV s⁻¹ in aqueous NaPF₆ solution.

nm)¹⁷ or PF₆⁻ (0.254 nm),¹⁷ but the shape of CF₃SO₃⁻ is different from spherical BF₄⁻ and PF₆⁻. Despite the differences, the electrochemical strain of PPy doped with CF₃SO₃⁻ was similar to those of the PPy doped with BF₄⁻ and PF₆⁻, although the mechanical elongation of the CF₃SO₃⁻-doped PPy was much larger. It seems that aromatic ester solutions of TBACF₃SO₃ gave a high molecular-weight PPy with less cross-linking, presumably because some interaction between pyrrole and CF₃SO₃⁻ depressed any undesirable side reactions, such as cross-linkage, a reaction at the 3-position of pyrrole, and termination.

Durability of Electrochemical Stretching of PPy Actuators Doped with CF₃SO₃⁻. As depicted in Figs. 1–4, the electrochemical strains for the second redox cycle at 2 mV s⁻¹ were smaller than those for the first redox cycle. The strains for the third and following cycles decreased slightly. Generally, the PPy actuators showing the maximum performance, such as the maximum strain and stress, are not very stable. Thus, practical devices based on CP actuators should be operated under mild conditions, such as 7% strain at 5 MPa.

As shown in Fig. 5a, the electrochemical strain of PPy doped with $CF_3SO_3^-$ for one redox cycle (the expansion-contraction ratio) at a faster scan rate of 50 mV s⁻¹ (0.0156 Hz) in an aqueous NaPF₆ solution (1.0 mol dm⁻³) remained almost constant at 6.7% up to 20 cycles. Note that very slow scan rate of 2 mV s⁻¹ for measuring the maximum electrochemical strain of a PPy actuator doped with $CF_3SO_3^-$; the first redox cycle gives the maximum strain (12.8%), whereas faster scan rates retard the peak of the electrochemical strain, because PPy

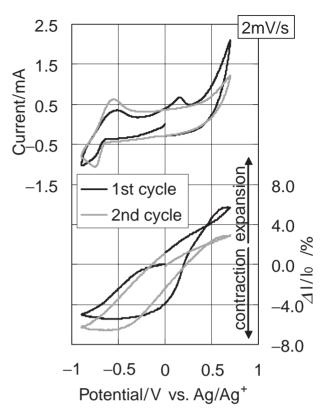


Fig. 3. A CV and an ECMD of a PPy film actuator prepared from a methyl benzoate solution of TBACF₃SO₃ on a Ti electrode, cycled between -0.9 V and +0.7 V at 2 mV s⁻¹ in aqueous NaPF₆ solution.

chains of the as-grown films cannot become disentangles for the first several cycles, triggered by the doping-dedoping of the dopant anions.

Figure 5b depicts the electrochemical strain of PPy doped with $CF_3SO_3^-$, driven by applying rectangular pulses at $\pm 0.7~V$ vs Ag/Ag^+ at 0.1 Hz in an aqueous NaPF₆ solution up to 100 cycles. The strain decreased very slightly to 3.3%, but was still usable. Further repeated electrochemical stretching of PPy- $CF_3SO_3^-$ occurred by applying rectangular pulses at $\pm 0.7~V$ vs Ag/Ag^+ (0.5 Hz at 6000 and 60000 cycles) in an aqueous NaPF₆ solution. It was found that the electrochemical strain remained 0.83% (64% of the first strain of 1.3%) and 0.48% (37%), respectively.

The durability of CPs has not yet been fully studied, and no solutions have been found. Also, that of CP actuators is also unknown. An improvement in the cycle life was attempted by using ionic liquids as the electrolyte to drive a PPy doped with PF_6^- . It was observed that stable electrochemical stretching (ca. 1.2%) up to 6000 cycles occurred in 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF_6) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI). However, all of the PPy actuators studied in our work required an aqueous solution to actuate. Thus, ionic liquids are not applicable to improve the cycle life of PPy actuators.

Electrochemical Contraction of PPy Films Doped with Various Anions. Figure 6 depicts the time course of the third electrochemical contraction of PPy films, prepared from a methyl benzoate solution of TBABF₄, TBAPF₆, TBACF₃SO₃,

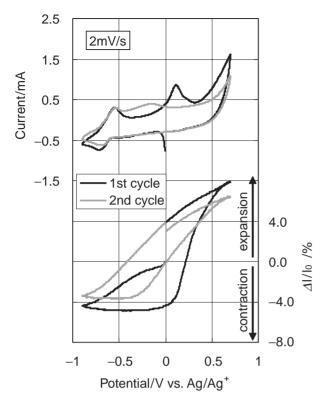


Fig. 4. A CV and an ECMD of a PPy film actuator prepared from a methyl benzoate solution of TBAClO₄ on a Ti electrode, cycled between -0.9 V and +0.7 V at 2 mV s⁻¹ in aqueous NaPF₆ solution.

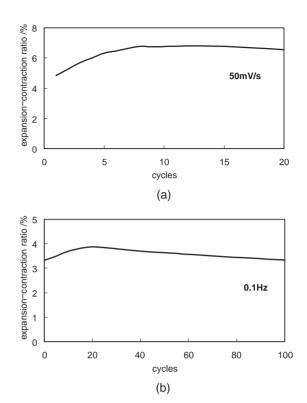


Fig. 5. Repeated electrochemical stretching of PPy films doped with $CF_3SO_3^-$, operated in aqueous solution of NaPF₆; (a) cycled between -0.9 V and +0.7 V vs Ag/Ag⁺ at 50 mV s⁻¹ and (b) driven by applying square pulse at ± 0.7 V vs Ag/Ag⁺ at 0.1 Hz.

Table 1. Electrochemical Strain and Stress, and Mechanical Properties of PPy Film Actuators Doped with Various Anions

	Dopant anions used for PPy preparation						
	BF ₄ -	PF_6^-	CF ₃ SO ₃ ⁻	ClO ₄ -			
Ionic radius ¹⁷ /nm	0.229	0.254	0.270	0.237			
Electrochemical strain/%	12.4	12.8	12.8	11.2			
Electrochemical stress ^{a)} /MPa	22.0	10.6	20.8	15.2			
Electrochemical stress ^{b)} /MPa	49.0	24.5	49.0	29.9			
Mechanical tensile strength/MPa	93.0	47.7	85.7	67.1			
Elongation/%	10–20	6–9	60-100	8-13			

Maximum electrochemical strain and stress were measured by sweeping potential between -0.9 V and +0.7 V vs Ag/Ag^+ at 2 mV s⁻¹, 10 mV s⁻¹ (a), and 100 mV s⁻¹ (b), respectively, in aqueous NaPF₆ solution.

and TBAClO₄, driven at -0.7 V vs Ag/Ag⁺ in NaPF₆ aq. at room temperature. Apparently, the order of the electrochemical contraction ratio was as follows: PPy-PF₆⁻ > PPy-CF₃SO₃⁻ > PPy-ClO₄⁻ > PPy-BF₄⁻. Since the anion (PF₆⁻) used for the electrochemical stretching was the same, the order of the contraction ratio should result in the packing of PPy films. Of the PPy film actuators doped with various anions, PPy-PF₆⁻ films were somewhat soft and the mechanical tensile strength (47.7 MPa) was smaller than those of the other PPy films. Therefore, the dopant anion of PF₆⁻ was easily expelled from the PPy-PF₆⁻ film. The other PPy films, however, were compact, mechanically strong, and looked similar, so that the order of the contraction ratio might be attributable to the anion size used for electropolymerization.

PPy Actuators Prepared with TBAClO₄. Since Otero et al. reported on the electrochemomechanical properties of PPy films prepared from an acetonitrile solution of LiClO₄, PPy films doped with ClO₄⁻ have been widely investigated as CP actuators. In the early stage of the research on CP actuators, it was difficult to measure linear actuation, due to the small electrochemical strain; thus, the bending motion of bilayer films was mainly studied. The volume change in PPy with various anions was estimated up to 3.4% with bending bilayers. The linear strains of a PPy doped with benzenesulfonate were directly measured, and a 1% strain was found in an acetonitrile/water (95/5) solution of sodium benzenesulfonate. Recently, we reported a 2.6–3.4% linear strain of PPy films, prepared from methyl benzoate, butyl benzoate, 1,2-di-

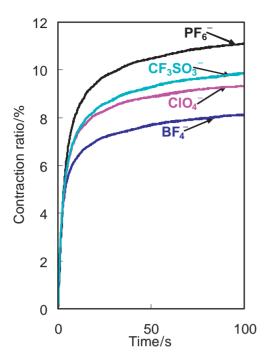


Fig. 6. Time-course of the third electrochemical contraction of PPy film actuators prepared from a methyl benzoate solution of TBAPF₆, TBACF₃SO₃, TBAClO₄, and TBABF₄, driven at −0.7 V vs Ag/Ag⁺ in aqueous solution of NaPF₆.

methoxyethane, 1-octanol, and propylene carbonate solutions of tetrabutylammonium benzenesulfonate, driven in an aqueous NaPF $_6$ solution. These results indicate that the conventional PPy actuators, including PPy doped with ${\rm ClO_4}^-$ and benzenesulfonate, exhibit moderate strains.

As depicted in Fig. 4, a PPy film prepared with TBAClO₄ as the electrolyte gave a similar CV and ECMD to those of the PPy films doped with BF₄ $^-$, PF₆ $^-$, and CF₃SO₃ $^-$. The electrochemical strain (11.2%) was unexpectedly larger than those of PPy actuators doped with ClO₄ $^-$, reported thus far. Table 2 gives the electrochemical strains for the first redox cycle of ClO₄ $^-$ -doped PPy films prepared in various solvents, and indicates that those prepared from aromatic ester solutions only gave a large electrochemical strain and stress, when driven in an aqueous NaPF₆ solution. Not only the ClO₄ $^-$ -doped PPy films, but also the BF₄ $^-$ - or CF₃SO₃ $^-$ -doped PPy prepared from an aromatic ester solution exhibited a large strain and stress. It therefore seems that aromatic esters gave PPy films

with a compact and well-entangled structure, suitable for powerful actuators with large strains.

As indicated in Table 2, the electrochemical strain of PPy-ClO₄ - prepared from a dimethyl phthalate solution of TBAClO₄ is slightly larger than that prepared from a methyl benzoate solution. A similar improvement in the electrochemical strain of PPy-BF₄⁻ was also observed, and 14.0% of the maximum electrochemical strain was achieved when prepared from a dimethyl phthalate solution of TBABF₄. The improvement in the electrochemical strain might be ascribed to the viscosity of the electrolytic solutions used for the electropolymerization of pyrrole. The growth of PPy chains on an electrode might occur more effectively in a more viscous solution of dimethyl phthalate to give PPy films with a more suitable conformation and packing of the chains, showing larger electrochemical strains. During the electrochemical polymerization of pyrrole, the PPy chains contained more solvent molecules, thus producing soft or less-compact films. Therefore, the electrochemical stress and the mechanical tensile strength may be slightly inferior to those prepared in methyl benzoate.

Electrochemical Stress of PPy Films Doped with Various Anions. As pointed out elsewhere, ¹⁰ the procedure used to evaluate the maximum stress induced electrically appeared to underestimate it because the procedure kept a considerably elongated state (doped state) of the PPy strip, the weakest state of the film, for a long time due to the slow scan rate of 10 mV s⁻¹. Therefore, the PPy film tended to break easily and the maximum stress was determined, even though the PPv strip was potentially able to pull up a heavier load. Figure 7 shows a correlation between the electrochemical stress and the contraction ratio of PPy actuators prepared from a methyl benzoate solution of TBACF₃SO₃ on a Ti electrode. At a scan rate of 10 mV s⁻¹, the PPy-CF₃SO₃⁻ film broke at about 21 MPa, whereas the PPy film pulled up the load to 49 MPa when cycled at 100 mV s⁻¹. In the case of a fast scan at 100 mV s⁻¹, the PPy strip did not break, but became unable to lift the load. This result suggests that the PPy-CF₃SO₃⁻ film exhibited the maximum electrochemical stress of 49 MPa, rather than 21 MPa, previously reported, and the value of 21 MPa was not the electrochemical stress of the PPy-CF₃SO₃⁻ film, but the mechanical tensile strength when the PPy-CF₃SO₃⁻ film was kept wet and doped for a long time. Similar increases in the maximum electrochemical stress were observed for PPy-BF₄⁻, PPy-PF₆⁻, and PPy-ClO₄⁻ actuators, as shown in Table 1. The electrochemical stresses reported thus far were therefore obviously underestimated by about one-half, and the maximum

Table 2. Electrochemical Strain and Stress, and Some Properties of PPy Actuators Doped with ClO₄⁻ Prepared from Various Solvents

	Solvents used for electropolymerization									
	MB	EB	BB	MP	EP	PC	BA/PC (4/1)	DME		
Electrochemical strain/%	11.2	11.2	11.7	13.5	12.2	8.2	_	11.1		
Electrochemical stress/MPa	15.2			12.3						
Mechanical tensile strength/MPa	67	60	66					36		
Mechanical elongation/%	10	13		18				7		
Electric conductivity/S cm ⁻¹	108	114	50	102	102	31	0.04	101		

MB: methyl benzoate; EB: ethyl benzoate; BB: butyl benzoate; MP: dimethyl phthalate; EP: diethyl phthalate; BA: *t*-butyl acetate; PC: propylene carbonate; DME: 1,2-dimethoxyethane.

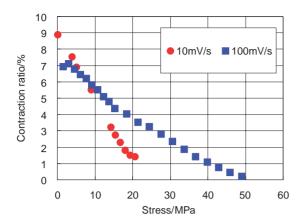


Fig. 7. The correlation between electrochemical contraction and electrochemical stress of PPy film actuators prepared from a methyl benzoate solution of TBACF $_3$ SO $_3$, cycled between -0.9 V and +0.7 V vs Ag/Ag $^+$ at 10 mV s $^{-1}$ and 100 mV s $^{-1}$.

stresses obtained by the novel procedure were about half of the mechanical tensile strength.

Table 1 indicates the maximum electrochemical stress and elongation of PPy films prepared from methyl benzoate solutions of TBABF₄, TBAPF₆, TBACF₃SO₃, and TBAClO₄. Clearly, PPy doped with CF₃SO₃⁻ solely elongated mechanically by up to 100% together with exhibiting a large mechanical tensile strength of 85.7 MPa. Using flexible and tough PPy-CF₃SO₃⁻ films, a number of practical CP actuator devices, such as an artificial muscle cell and a diaphragm pump, can be fabricated.¹²

Conclusion

Of the polypyrrole film actuators doped with BF_4^- , PF_6^- , $CF_3SO_3^-$, and CIO_4^- , exhibiting a large electrochemical strain of more than 10%, PPy doped with $CF_3SO_3^-$ film was flexible and tough. It is therefore more suitable for fabricating practical actuator devices, presumably because the interaction between the pyrrole rings and the dopant is strong, and the degree of polymerization of the PPy doped with $CF_3SO_3^-$ film is larger than those of the other PPy films. In appropriate measurements of the electrochemical stress of PPy film actuators, electrochemical stresses up to 49 MPa were observed, which were almost twice as large as those previously reported. Such a large electrochemical stress (49 MPa) and mechanical tensile

strength (86–93 MPa) of the PPy film actuators doped with BF_4^- and $CF_3SO_3^-$ were also attributable to the strong interaction between PPy chains, together with the interaction between the pyrrole rings and the dopant anions. Artificial muscles, such as PPy film actuators, were stable under moderate conditions, similarly to natural muscles. Thus, practical devices using PPy actuators should be operated under mild conditions, such as moderate strain (up to 7%) and stress (up to 5 MPa).

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