SHORT COMMUNICATIONS

Gel-like Polypyrrole Based Artificial Muscles with Extremely Large Strain

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Conducting polymers (CPs) such as polypyrrole (PPy), polythiophene, and polyaniline change in volume triggered by the insertion and the release of dopant, and have been expected as artificial muscles.[1–4] Improvement in the electrochemical strain and stress has been mainly tackled for decades, and almost reached the practical level.[5] The electrochemical stress up to 49 MPa of PPy based CP actuators,[6] prepared with TBABF$_4$ or TBACF$_3$SO$_3$ as the electrolyte from an aromatic ester solution, has aroused interest of engineers who desire to obtain powerful actuator materials. Moreover, as electrically induced force can be tailored by using multi-wound PPy film actuators[5] and bundles of PPy–metal coil composite actuators,[7] applications of the powerful CP actuators have become realistic.

In contrast to the powerful CP actuators, highly stretchable CP actuators should also be desirable actuator materials for the engineers. The moderate electrochemical strain (1–3%)[1,2,8] used to be one of the fatal disadvantages for CP actuators, and such a small strain made it difficult for the engineers to fabricate practical actuator devices by using the CP actuators. A CP actuator with large electrochemical strain is therefore one of the most important targets in the technology of the CP actuators. Madden *et al.* reported a novel thiophene based CP molecular actuator with calyx[4]arene hinges, generating strains of 20% or more at stress in excess of 0.5 MPa.[9,10] Bay *et al.* indicated that an addition of a compliant gold electrode (50–100 nm) to one of the surfaces of PPy doped with dodecylbenzenesulfonate improved the strain up to 12%.[11] We prepared highly stretchable and powerful PPy actuators exhibiting the strain up to 15% at 0.1 MPa, and 7% at a considerably large load of 5 MPa.[5] The PPy actuators can be obtained by using a simple current-constant electropolymerization from a methyl benzoate solution of TBABF$_4$ or TBACF$_3$SO$_3$ on a Ti electrode. Although these were the first CP actuators able to show a large strain and stress induced electrically, the strain was far below that (20–40%) of natural muscles.[12]

Recently, we have found a PPy film prepared electrochemically with tetrabutylammonium bis(trifluoromethanesulfonyl)imide, TBA(CF$_3$SO$_2$)$_2$N (TBATFSI) as the electrolyte, exhibiting the electrochemical strain up to 26.5% in aqueous LiTFSI solution.[13] The extremely large strain was due presumably to the large TFSI anion which can easily go in and out of the TFSI-doped PPy film as dopant. Further investigation on PPy actuators prepared and driven with TFSI derivatives, (C$_n$F$_{2n+1}$SO$_2$)$_2$N$^-$, as artificial muscles whose strain is equivalent to that of natural muscles will be described in this paper.
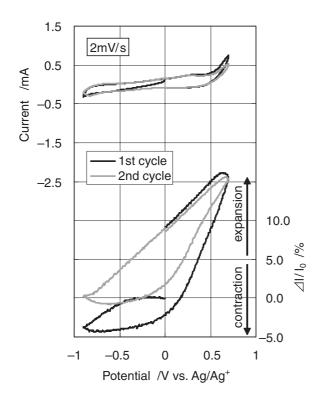
EXPERIMENTAL

Electrochemical polymerization of pyrrole was performed in a one-compartment two-electrode cell at 0 °C for 6 h from a methyl benzoate solution of Li(C$_n$F$_{2n+1}$SO$_2$)$_2$N (0.2 mol dm^{-3}) (n = 1–4). When a PPy film deposited on Pt or Ti was immersed in an acetone bath to peel it off the electrode, the PPy film swelled considerably in acetone. The film shank when dried in air. The electrochemomechanical deformation (ECMD) of a free-standing PPy film (2 mm × 15 mm) was measured in a three-electrode cell with a pinhole at the bottom through which a W wire passed to suspend a load (typically 0.1 MPa for measuring the maximum electrochemical strain). The electrolytic solutions for driving PPy actuators were aqueous or propylene carbonate (PC) solutions of Li(C$_n$F$_{2n+1}$SO$_2$)$_2$N

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(0.5 mol dm^{-3}) ($n = 1$–4). Detail of the procedure was described elsewhere.[5,13]

RESULTS AND DISCUSSION

Figure 1 depicts a cyclic voltammogram (CV) and an electrochemomechanical deformation (ECMD) of PPy film prepared from a methyl benzoate solution of lithium bis(pentafluoroethanesulfonyl)imide (Li-(C$_2$F$_5$SO$_2$)$_2$N) (LiPFSI) (0.2 mol dm^{-3}), cycled between -0.9 V and $+0.7$ V *vs.* Ag/Ag$^+$ at 2 mV s^{-1} in aqueous LiPFSI solution (0.5 mol dm^{-3}). Contraction and expansion with dedoping and doping of PFSI anion were observed on applying cathodic and anodic potentials, respectively. The electrochemical strain for the first redox cycle was 20.9%, larger than that (16.7%) of TFSI-doped PPy driven similarly in LiTFSI aq. The result strongly suggests that the larger the size of bis(perfluoroalkanesulfonyl)imide anion used, the larger the electrochemical strain should be observed. As can be seen in Figure 1, the PFSI-doped PPy did not elongate completely on oxidation probably because PFSI anion is too large to penetrate deeply into the PFSI-doped PPy film. When cycled much more slowly at 0.2 mV s^{-1}, the electrochemical strain of PFSI-doped PPy was 29.2%, larger than that (22.9%) of PPy prepared with LiTFSI as the electrolyte at the same scan rate. Note that the electrochemical strains of TFSI-doped PPy, prepared with tetrabutylammonium salt

(TBATFSI), cycled at 2 mV s^{-1} and 0.2 mV s^{-1} in aqueous LiTFSI solution were 20.1% and 26.5%, respectively,[13] as the voltage increased too high during the electrochemical polymerization due to the low ionic conductivity of methyl benzoate solution of Li(C$_n$F$_{2n+1}$SO$_2$)$_2$N, and therefore the electrochemical strains of PPy–(C$_n$F$_{2n+1}$SO$_2$)$_2$N$^-$ prepared with Li salts were smaller than those prepared with TBA salts. As tetrabutylammonium bis(heptafluoropropanesulfonyl)imide (TBAHFSI) or tetrabutylammonium bis-(nonafluorobutanesulfonyl)imide (TBANFSI) was not commercially available, we used Li salts for the preparation of all the PPy–(C$_n$F$_{2n+1}$SO$_2$)$_2$N$^-$ ($n = 1$–4) films in this work although we have been mainly using TBATFSI and TBAPFSI for preparing PPy–(C$_n$F$_{2n+1}$SO$_2$)$_2$N$^-$ ($n = 1$–2).

The very large electrochemical strain of PFSI-doped PPy was attributable to the fact that large PFSI anions were able to penetrate into and emerge from the PFSI-doped PPy film that possessed a macro-porous morphology (see the graphical abstract), similar to that of the TFSI-doped PPy film.[13] The PFSI-doped PPy film as well as the TFSI-doped PPy film had gel-like characteristics, that is, the TFSI-doped PPy film swelled considerably in some organic solvents such as acetone (178% in area), propylene carbonate (PC) (165%), and 1-methyl-2-pyrrolidone (NMP) (230%). These solvents are therefore good solvents for the TFSI-doped PPy.
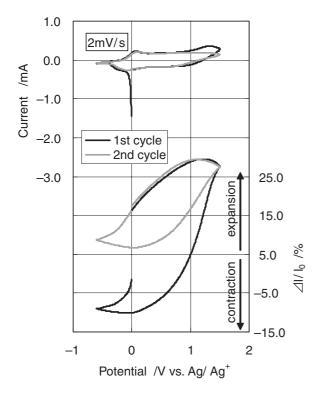
As indicated in Table I, bis(heptafluoropropanesulfonyl)imide (HFSI) and bis(nonafluorobutanesulfonyl)imide (NFSI)-doped PPy films showed 11.9% and 2.95% strain, driven in LiHFSI and LiNFSI aq. (0.5 mol dm^{-3}), respectively, cycled at 2 mV s^{-1}. The disappointedly small electrochemical strains resulted from the too large HFSI and NFSI anions. Even at a scan rate of 0.2 mV s^{-1}, the strains of HFSI and NFSI-doped PPy films were 19.4% and 8.36%, respectively, much smaller than those of TFSI and PFSI-doped PPy films. It appears that the HFSI and NFSI anions can no longer penetrate into PPy chains lightly swollen in aqueous solution.

Figure 2 shows a CV and an ECMD of NFSI-doped PPy, cycled between -0.6 V and $+1.5$ V *vs.* Ag/Ag$^+$ at 2 mV s^{-1} in PC solution of LiNFSI (0.5 mol dm^{-3}). On applying potential to -0.6 V, the NFSI-doped PPy film shortened by 10.2% with dedoping of NFSI anion, and elongated with doping of NFSI when potential was swept to $+1.5$ V. The electrochemical strain for the first redox cycle was 39.6%, the largest linear electrochemical strain of CP actuators ever reported. The NFSI-doped PPy swelled massively in PC, and thus the large NFSI anions became possible to go out and into the NFSI-doped PPy film, exhibiting the large strain. The electrochemical strain for

Figure 1. A CV and an ECMD of PPy doped with PFSI, cycled between -0.9 V and $+0.7$ V *vs.* Ag/Ag$^+$ at 2 mV s^{-1} in aqueous LiPFSI solution (0.5 mol dm^{-3}).

Table I. The electrochemical strain and stress, and mechanical tensile strength of PPy actuators prepared from methyl benzoate solution of $Li(C_nF_{2n+1}SO_2)_2N$ ($n = 1–4$) (0.2 mol dm^{-3})

	Scan rate /mV s^{-1}	Solvent	$Li(C_nF_{2n+1}SO_2)_2N$			
			$n = 1$	2	3	4
Electrochemical strain/%	2	H$_2$O	16.7	20.9	11.9	2.95
	0.2	H$_2$O	22.9	29.2	19.4	8.36
	2	PC	23.3	30.0	34.6	39.6
Electrochemical stress/MPa	10	H$_2$O or PC	10.5 (H$_2$O)		2.1 (PC)	1.9 (PC)
Mechanical tensile strength/MPa (dry)			37		5–10	4–13
Thickness/µm			30	29	30	51
Conductivity/S cm^{-1}			71.7	45.7	28.1	39.3

The actuators were mainly cycled between -0.9 V and $+0.7$ V *vs.* Ag/Ag$^+$ at 10, 2, or 0.2 mV s^{-1} in respective aqueous $Li(C_nF_{2n+1}SO_2)_2N$ solution (0.5 mol dm^{-3}). When driven in PC solution of $Li(C_nF_{2n+1}SO_2)_2N$, potential was swept between -0.6 V and $+1.5$ V *vs.* Ag/Ag$^+$.

Figure 2. A CV and an ECMD of PPy doped with NFSI, cycled between -0.6 V and $+1.5$ V *vs.* Ag/Ag$^+$ at 2 mV s^{-1} in PC solution of LiNFSI (0.5 mol dm^{-3}).

the second redox cycle decreased to 22.8% presumably because loosely packed PPy chains of the as-grown NFSI-doped PPy film cannot revert to the original conformation after the redox cycle with doping and dedoping of NFSI. The third and the following cycles did not show such a large decrease in the electrochemical strain. The order of electrochemical strain for $(C_nF_{2n+1}SO_2)_2N^-$-doped PPy in PC solution of $Li(C_nF_{2n+1}SO_2)_2N$ was as follows:

$$NFSI > HFSI > PFSI > TFSI$$
$$39.6 \quad 34.6 \quad 30.0 \quad 23.3 \quad (\%).$$

Clearly, the order corresponded to the size of dopant

anion; $(C_nF_{2n+1}SO_2)_2N^-$.

The measurement of electrochemical strain of $(C_nF_{2n+1}SO_2)_2N^-$-doped PPy actuators mentioned above was performed using the respective Li-$(C_nF_{2n+1}SO_2)_2N$ as the electrolyte. The same anion was found suitable for the electrochemical stretching of the $(C_nF_{2n+1}SO_2)_2N^-$-doped PPy actuators. When aqueous LiPFSI solution was employed for measuring the electrochemical strain of the TFSI-doped PPy, the PPy film hardly elongated on applying anodic potential, exhibiting 1.5% strain probably because the PFSI anion is too large to penetrate into the TFSI-doped PPy film. A similar phenomenon was already reported when a PPy film doped with $CF_3SO_3^-$ was driven electrochemically in aqueous LiTFSI solution.[13] It is thought that $(C_nF_{2n+1}SO_2)_2N^-$ anion used for the electrochemical polymerization of pyrrole should be the same as that used for the electrochemical stretching of the PPy film obtained. During the electropolymerization of pyrrole with $(C_nF_{2n+1}SO_2)_2N^-$ anion, loosely packed PPy chains were formed with $(C_nF_{2n+1}SO_2)_2N^-$ as the template, and therefore the $(C_nF_{2n+1}SO_2)_2N^-$-doped PPy actuated effectively only with the same $(C_nF_{2n+1}SO_2)_2N^-$ anion as dopant. The $(C_nF_{2n+1}SO_2)_2N^-$-doped PPy actuator hardly elongated with larger anions as mentioned earlier, and elongated ineffectively with smaller anions as described elsewhere.[13]

Table I also indicates the electrochemical stress and the mechanical tensile strength of the PPy film doped with $(C_nF_{2n+1}SO_2)_2N^-$. As pointed out in previous papers,[13,14] a negative correlation between the electrochemical strain and stress, and a positive correlation between the electrochemical stress and the mechanical tensile strength of the $(C_nF_{2n+1}SO_2)_2N^-$-doped film were observed. The larger the anion size, the smaller the electrochemical stress and the mechanical strength of the $(C_nF_{2n+1}SO_2)_2N^-$-doped PPy film because of the looser packing and entanglement of PPy chains.

In conclusion, novel CP actuators based on PPy

doped with $(C_nF_{2n+1}SO_2)_2N^-$ were prepared electro-chemically. The PPy actuators exhibited extremely large electrochemical strain up to 40% with moderate stresses. The larger the size of bis(perfluoroalkanesul-fonyl)imide anion, $(C_nF_{2n+1}SO_2)_2N^-$, the larger the electrochemical strain was observed. The reason why such a large anion worked as dopant was that the PPy film swelled enough to introduce and expel the large anion when driven in PC solution as if it were a gel polymer. Two PPy actuators, the exceed-ingly stretchable PPy actuators doped with $(C_nF_{2n+1}SO_2)_2N^-$ and the powerful PPy actuators doped with $CF_3SO_3^-$, having quite different charac-teristics should make CP actuators practical as artifi-cial muscles, and hopefully many products composed of the PPy actuators will be developed soon. The study on the durability and the fast response of the PPy actuators, and practical applications are currently underway.

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