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Free-standing polypyrrole actuators with response rate of 10.8% s^{-1}

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Abstract

A free-standing polypyrrole (PPy) film actuator without any additional electrode or metal backing, prepared electrochemically from an aromatic ester solution of tetra-*n*-butylammonium bis(trifluoromethanesulfonyl)imide (TBATFSI), exhibited up to 29% electrochemical strain, and a peak response rate of 10.8% s^{-1} in an H_2O/propylene carbonate (PC) solution of LiTFSI. This is the very first time both large electrochemical strains and fast response rates were achieved in the conducting polymer actuators. The large and fast electrochemical deformation resulted from the fact that the PPy film doped with large TFSI anions swelled in PC such that TFSI can insert and expel the PPy film easily, and that a high ionic conductivity in H_2O/PC solution enabled to move TFSI quickly.

Keywords: Fast response rate; Polypyrrole actuator; Artificial muscle; Conducting polymer; Bis(trifluoromethanesulfonyl)imide

1. Introduction

Conducting polymers (CPs) such as PPy are promising soft actuator materials potentially applicable to artificial muscle devices because of their large electrochemical stresses (3–5 MPa) [1–4], 10 times as large as that (0.35 MPa) [5] of mammalian skeletal muscles. The applications of CP linear actuators have been, however, quite limited due to their moderate electrochemical strains (1–3%) [1,2,6]. Recently, some PPy actuators with more than 10% electrochemical strains appeared [7–12], and some of which achieved up to 40% strain [11,12], almost same level as that of skeletal muscles. Such extremely large electrochemical strains were measured when potential was swept at very slow scan rates of 2 or 0.2 mV s^{-1}. Obviously, most applications of CP actuators require much faster response rates, so CP actuators with large strains and fast response rates are highly expected.

We reported recently the improvement in the response rate of TFSI-doped PPy actuators by using H_2O/PC mixed solutions of LiTFSI instead of aqueous or PC solutions as the electrolytic solution for driving the PPy-TFSI film actuators [12]. The novel procedure to operate the PPy-TFSI actuators would make it possible to fabricate artificial muscle devices with an extremely large displacement and a fast response. This paper describes how and why the fast response rate of PPy-TFSI film actuators was achieved.

2. Experimental

PPy films were prepared electrochemically at 0.2 or 0.1 mA cm^{-2} from 0.25 mol dm^{-3} pyrrole and 0.2 mol dm^{-3} TBATFSI in aromatic esters such as methyl benzoate (MB) and dimethyl phthalate (MP) on a Pt or Ti electrode (effective surface area: 10 and 200 cm^2, respectively) for 4 or 8 h at 0 or −10 °C. The films obtained (thickness: 15–60 μm, conductivity: 60–140 S cm^{-1}) were peeled off the electrode, rinsed with acetone, and air-dried. As reported previously [10,11], the TFSI-doped PPy films swelled in acetone and shrank on drying [13]. The PPy film was cut into a 10 mm × 2 mm strip and set in a one-compartment three-electrode cell described

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elsewhere [8] to measure change in length of the PPy strip by using a laser displacement meter (KEYENCE LE-4000) at typically 0.1 MPa load (under isotonic conditions) on applying potential. The definition of electrochemical strain of PPy actuators was change in length of the strip divided by the original length ($\Delta l/l_0$). When the maximum strain was measured, potential was swept between −0.9 and +0.7 V versus Ag/Ag^+ by using a potentio-galvanostat (Princeton Applied Research 263A) at 2 mV s^{-1} in H_2O/PC solutions of LiTFSI. Electrochemical contraction and expansion were conducted by applying a constant potential of −0.7 and +0.7 V versus Ag/Ag^+, respectively, for 100 s except the second expansion (30 s) at room temperature. Repeated electrochemical stretching was carried out by using a Hokuto Denko HA-151 potentio-galvanostat and a Wave Factory WF1946 multifunction synthesizer.

3. Results and discussion

Fig. 1 shows the electrochemical contraction of a TFSI-doped PPy film actuator (thickness: 35 μm, conductivity: 61 S cm^{-1}), prepared electrochemically at 0.1 mA cm^{-2} from an MP solution of TBATFSI for 8 h on a Pt electrode at −10 °C, driven at −0.7 V versus Ag/Ag^+ in an H_2O/PC (60/40) solution of LiTFSI. Note that this was not the first but the third contraction, so two contraction–expansion cycles for 330 s in total was performed before this contraction. The free-standing PPy-TFSI film actuator contracted rapidly exhibiting a peak response rate of 10.8% s^{-1}. The peak response rate was much larger than that (ca. 0.1% s^{-1}) of other conventional PPy actuators [2], and that (3.2% s^{-1}) of a PF_6^--doped PPy by using resistance compensation techniques [14]. Ding et al. [15] prepared a tubular PF_6^--doped PPy with a Pt helical wire, exhibiting up to 13% s^{-1} strain rate and 5% strain, and we reported a PPy film with a compliant Au electrode at one side, prepared from an MB solution of $TBACF_3SO_3$, showed a peak strain rate of 8.8% s^{-1} and the maximum strain of 12.1% [16]. Additional metal electrodes such as the Pt helical wire and the compliant Au thin layer decreased the voltage drop along the PPy actuators, giving fast response rates.

Without any additional electrode or metal backing, the free-standing PPy film doped with TFSI described in this paper exhibited a peak response rate of 10.8% s^{-1} together with the maximum strain of 23.6% measured at a slow scan rate of 2 mV s^{-1} in an H_2O/PC (60/40) solution of LiTFSI, and therefore would be a promising candidate for artificial muscle devices with a fast response rate and a large electrochemical deformation. The electrochemical contraction ratios of the PPy-TFSI film for 2, 5, 10, and 100 s were 14.9, 20.6, 22.7, and 25.8%, respectively, as shown in Fig. 1 except for 100 s, much faster than driven in aqueous solution of LiTFSI where 4.6, 7.5, 9.2, and 12.6%, respectively, were observed. In order to design and fabricate practical actuator devices, it would be convenient to use the contraction ratio for 2 and 10 s as an indication of the response speed rather than a peak response rate, and therefore the contraction ratio for 2 and 10 s will be shown hereinafter.

Fig. 2 depicts the electrochemical contraction ratios for 2 and 10 s in the third contraction, and the maximum electrochemical strains measured at 2 mV s^{-1} of PPy-TFSI film actuators in H_2O/PC mixed solutions of LiTFSI (PC contents: 0, 25, 40, 50, 75, and 100%). The electrochemical contraction occurred more rapidly in H_2O/PC mixed solutions of LiTFSI than in aqueous or PC solution. PPy films doped with TFSI swelled in PC by 65% in area [11], resulting in a smoother transfer of large TFSI anions in PPy in H_2O/PC mixed solutions than in aqueous solution. Due to a lower ionic conductivity of 100% PC solution of LiTFSI, the response speed was slower in PC. Therefore, the PC content of 40% resulted in the fastest response rate in this particular case. Preliminary experiments indicated that the best PC contents were different when other dopants such as bis(pentafluoroethanesulfonyl)imide, $(C_2F_5SO_2)_2N^-$, were used, and that some other organic solvents such as γ-butyrolactone can be used to increase the response rate instead of PC.

It should be pointed out that not only the electrochemical response rates of the PPy-TFSI film actuator but also

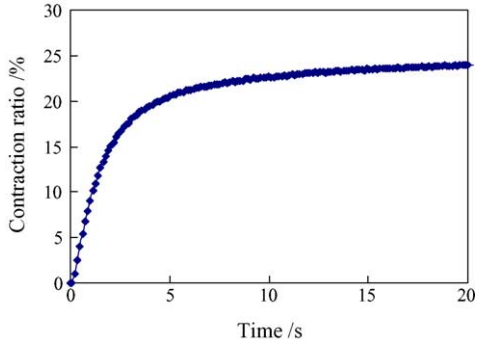

Fig. 1. The electrochemical contraction of a PPy-TFSI film actuator driven in an H_2O/PC (60/40) solution of LiTFSI at a constant potential of −0.7 V vs. Ag/Ag^+ at room temperature.

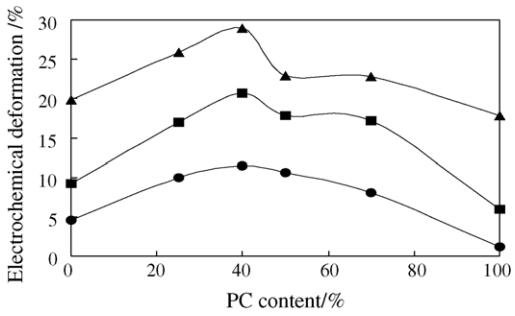

Fig. 2. The contraction ratios for 2 s (●) and 10 s (■), and the maximum strains (▲) of PPy-TFSI film actuators driven in H_2O/PC solutions of LiTFSI at a constant potential of −0.7 V, and cycled between −0.9 and +0.7 V vs. Ag/Ag^+ at 2 mV s^{-1}, respectively.

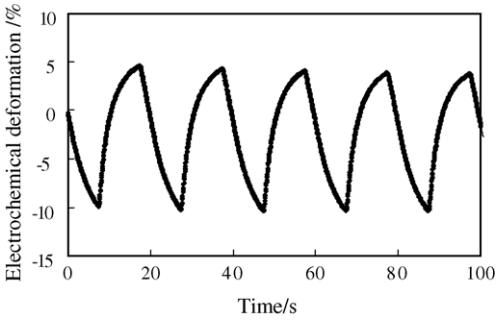

Fig. 3. Repeated electrochemical stretching of a PPy-TFSI film actuator driven in an H_2O/PC (60/40) solution of LiTFSI at a constant potential of ±0.7 V vs. Ag/Ag^+.

the maximum electrochemical strains in H_2O/PC mixed solutions of LiTFSI were larger than those measured in aqueous or PC solution. A PPy film, prepared similarly from an MB solution of TBATFSI, exhibited the maximum electrochemical strains of 20.1 and 26.5% when cycled at 2 and 0.2 mV s^{-1}, respectively [10], whereas the maximum electrochemical strain of 28.9% at 2 mV s^{-1} in an H_2O/PC (60/40) solution shown in Fig. 2 did not increase even when cycled at 0.2 mV s^{-1}. This result suggests that the PPy-TFSI film driven in an H_2O/PC (60/40) solution swelled enough to withdraw the maximum performance of the electrochemical strain even cycled at 2 mV s^{-1}. Large TFSI anions could not easily go into and out of the PPy-TFSI film which did not swell much in aqueous solution, and it would take more time to reach equilibrium.

Fig. 3 depicts repeated electrochemical stretching of a PPy-TFSI film actuator, prepared from an MP solution of TBATFSI, driven in an H_2O/PC (60/40) solution of LiTFSI at ±0.7 V versus Ag/Ag^+ at 0.05 Hz (10 s for each elongation or contraction). The PPy actuator showed stable and large (ca. 15%) electrochemical stretching at 0.05 Hz [17]. Such large and fast electrochemical deformation would arouse engineers' attention to fabricate practical artificial muscle devices. We would like to demonstrate some devices using the extremely stretchable TFSI-doped PPy actuator shown in this paper, similarly to those prepared with the powerful $CF_3SO_3^-$-doped PPy actuators such as diaphragm pumps [18], PPy-metal coil composites (artificial muscle fibres) [19] and PPy-zigzag metal wire composite films [20].

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