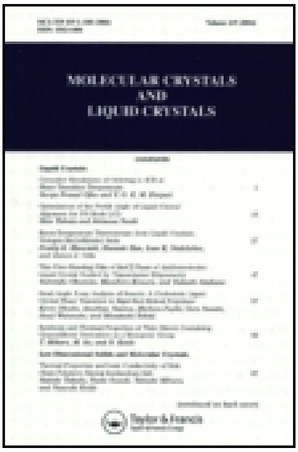

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Dynamic Behaviors of Polypyrrole Actuators in Electrolyte Solution Mixed with 2-Propanol

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It has been previously reported that dynamic behaviours of polypyrrole (PPy) soft actuators were improved when they were driven in aqueous solutions of an electrolyte, lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) containing an optimised amount of 2-propanol. In this work, the influences of the potential sweep rate on electrochemical and creep strains of PPy actuators in aqueous LiTFSI electrolyte solutions with 2-propanol concentrations of 0 and 20% were investigated under the load stress of 0.3 MPa. The electrochemical strain rates in the 0% and 20% 2-propanol solution were found to be approximately 0.1%s^{-1} and 0.25%s^{-1}, respectively, and they are nearly independent of the sweep rate between 10 and 25 mVs^{-1}. These results suggest that TFSI anion penetration into the PPy films might be limited by the interactions between the PPy surface and the TFSI anions. The creep rate was more rapidly increased as time elapsed in the electrolyte solution containing 2-propanol than that in the electrolyte solution without 2-propanol, which was due to the swelling of PPy film in the electrolyte.

Keywords LiTFSI; polypyrrole; 2-propanol; soft actuator

1. Introduction

Organic soft actuators made of conducting polymers such as polypyrrole (PPy) films are of special interest for application in microelectromechanical systems (MEMS) because they generate fairly large electrochemical stresses between 3 and 5 MPa [1–5]. Their electrochemical strains were between 1 and 3%. Recently, it has been reported that some PPy actuators exhibit strains of more than 10% [6–11], and that some of those even achieved up to 40% of the strain [11]. The improved strain has been mostly achieved using an electrolyte of tetra-n-butylammonium bis(trifluoromethansulfonyl)imide (TBATFSI) during PPy electropolymerization. These actuators generally function under a low potential voltage range less than 1 V.

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Hara *et al.* reported that their TFSI-doped porous PPy films exhibited increased deformation when their aqueous lithium bis(trifluoromethansulfonyl)imide (LiTFSI) electrolyte solutions contained propylene carbonate [12]. They attributed those effects to the swelling of the PPy film caused by the penetration of propylene carbonate. The swelled PPy film could more easily pass TFSI anions. Hoshino *et al.* also tried to immerse TFSI-doped PPy films into several organic chemicals, and found that the PPy films showed notable swelling in 2-propanol. They reported that the PPy actuators showed the increased electrochemical strains in aqueous LiTFSI solutions containing 20 to 40% of 2-propanol [13]. In this paper, the dynamic electrochemical deformation characteristics of TFSI-doped PPy soft actuators under potential sweep rates between 10 and 25 mV s^{-1} in aqueous LiTFSI solutions with different 2-propanol concentrations are reported.

2. Experimental Procedure

The polymerization of PPy films was carried out using a computer-controlled potentio-galvanostat (Hokuto Denko HZ-5000). A counter electrode (Ti), a reference electrode (Ag/AgCl), and a working electrode (Ti) were immersed into methyl benzoate solutions of 0.25 M pyrrole and 0.2 M N,N-diethyl-N-methyl-N-(2-methoxyethyl)-ammonium bis(trifluoromethanesulfonyl)imide, and the potential voltage was controlled to keep a constant current of 0.2 mA cm^{-2} for 4 h at 20°C between the counter electrode and the working electrode. The thickness of the PPy films was measured to be approximately 150 μm using a micrometer. The obtained films were peeled off from the electrode, rinsed with acetone, and dried in air. The PPy films were cut into $20 \times 5\,\mathrm{mm}^2$ strips to form the PPy actuators.

The actuator characterization system that utilizes a balance to measure the expansion and contraction ratios under a load stress was described elsewhere [14,15]. The PPy actuator was used as the working electrode in the 1 M LiTFSI aqueous electrolyte solutions containing 2-propanol concentrations of 0 and 20%. Both of the PPy actuator ends were clipped with two metal plates. The PPy actuator exhibited the expansion and contraction motions under the alternating potential with the triangular wave shape applied between the PPy actuator and the counter electrode. The potential voltage difference between the PPy actuator and the electrolyte solution was monitored using the Ag/AgCl reference electrode. The peak values of the potential voltage were -1 and $+1$ V, and the potential sweep rates were 10, 20, and 25 mV s^{-1}. The extension and contraction of the PPy actuator was measured by monitoring the displacement of the weight position using a laser displacement sensor (Keyence LE-4000). Moreover, a load stress of 0.3 MPa was applied on the PPy actuator by placing corresponding weights on the saucer of the balance.

3. Results and Discussion

Figure 1 shows the time dependences of the strain of the actuators, as measured by the displacement of the weight as a function of time under the load stress of 0.3 MPa. The strain in Figure 1 was defined as the length change of the PPy actuators divided by the length prior to deformation. No potential voltage was given for the first 30 s, and after that repeated voltage sweeps with a period of 400 seconds at the potential sweep rate of 10 mV s^{-1} were applied to the PPy actuators. The

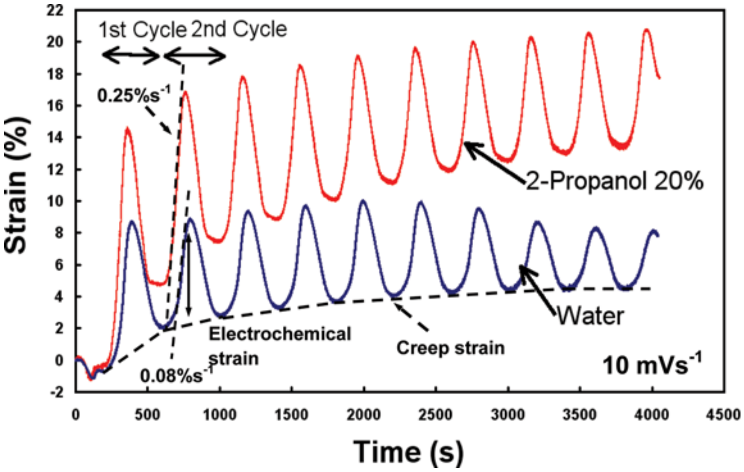

Figure 1. Relationships between the strain of the actuator and time under the repeated operation of the actuator for 10 times with the potential sweep rate of 10 mV s^{-1}. The actuators were electrochemically deformed in aqueous solutions of 1 M LiTFSI mixed with 2-propanol concentrations of 0 (water) and 20%. The load stress during the deformation was 0.3 MPa.

characteristics of the actuators were measured in aqueous solutions of LiTFSI with the different 2-propanol concentrations of 0 (water) and 20%. During the initial 130 s of the first cycle, the PPy actuators immersed in the electrolyte solutions with the 2-propanol concentrations of 0 and 20% showed slight reduction of the PPy length. Here, it should be noted that the strain of the measured PPy actuator consists of the electrochemical strain caused by anion motions and the swelling (creep) strain. Therefore, the electrochemical strain was defined by the difference of the peak value minus the lowest values of the strain for each potential cycle. The electrochemical strain of the PPy actuator driven in the 0% 2-propanol electrolyte for the second cycle exhibited nearly 7%. In contrast, the electrochemical strain of the PPy actuator driven in the aqueous solution of LiTFSI containing 20% of 2-propanol was 12%. In this case, the electrochemical strain of the PPy actuator gradually decreased after the repeated potential cycles but it stayed around 10%, while the creep strain of the actuators continuously increased. This creep strain of the PPy actuator in the 20% 2-propanol electrolyte was larger than that in the 0% 2-propanol (water) electrolyte. This seems to suggest that the creep strain is larger in the former case due to the swelling of the PPy film in 2-propanol. These creep behaviors look similar to creep effects in metal deformation processes. Sendai *et al.* recently reported in their detailed study on creep effects of PPy actuators, and concluded that this elongation could be recovered by releasing the stress during the deformation [15]. Hence, they called this phenomenon the memory effect. The dotted straight lines correspond to the tangents of the second peaks, and the tangential slopes correspond to the electrochemical strain rate of 0.25% s^{-1} for the actuator in the 20% 2-propanol electrolyte and 0.08% s^{-1} for the actuator in the 0% 2-propanol (water) electrolyte, respectively.

Figure 2 shows the cyclic voltammograms for PPy actuators in the LiTFSI electrolyte solutions with 0 and 20% of 2-propanol under the potential sweep rate of 10 mV s^{-1}. It is evident that the PPy actuator in the LiTFSI solutions with the concentration of 20% 2-propanol exhibited much larger hysteresis than that in

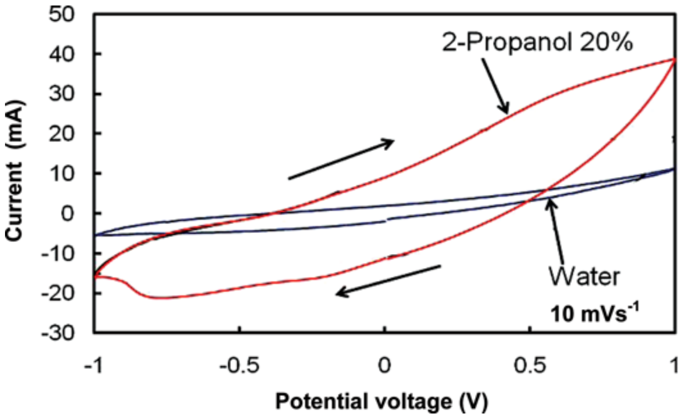

Figure 2. Cyclic voltammograms for PPy actuators in LiTFSI solutions 0 (water) and 20% of 2-propanol with the potential sweep rate of 10 mV s^{-1}.

the LiTFSI solutions with the concentration of 0% 2-propanol. This means that the TFSI$^-$ anions and the Li$^+$ cations were more rigorously diffusing into or out of the PPy film immersed in the LiTFSI electrolyte solution with the concentration of 20% 2-propanol than in the LiTFSI electrolyte solution with the concentration of 0% 2-propanol.

It is interesting to investigate whether the response time of the PPy actuator improves when the potential sweep rate is increased. Figure 3 shows the potential sweep rate dependences of the electrochemical strain of the PPy actuators in the electrolyte solutions with 0 and 20% 2-propanol. The electrochemical strains continuously decreased with the sweep rate. The electrochemical strain of the PPy actuator in the electrolyte solution with 20% 2-propanol is larger than those in the electrolyte solution with 0% 2-propanol in the sweep rate range between 10 and 25 mV s^{-1}.

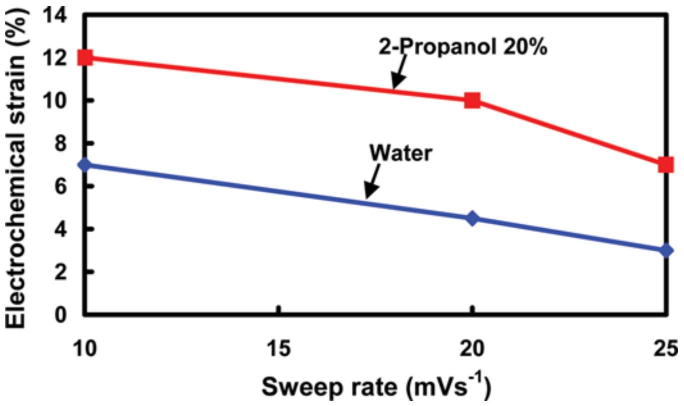

Figure 3. Sweep rate dependences of electrochemical strains for PPy actuators in LiTFSI solutions with 2-propanol concentrations of 0 (water) and 20%.

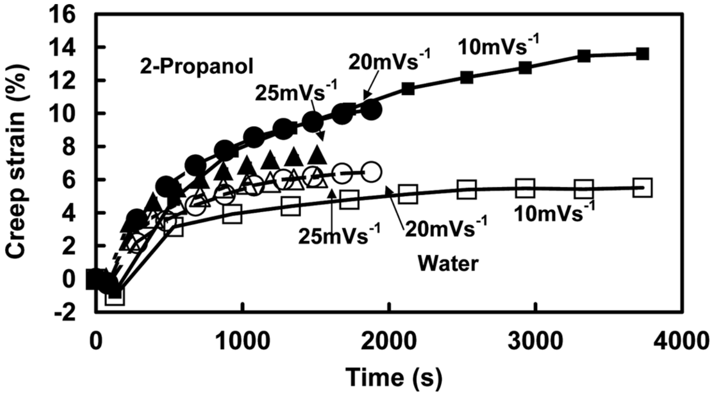

Figure 4. Comparison of creep strains for PPy actuators driven in LiTFSI solutions 0 (water) and 20% of 2-propanol with different potential sweep rates.

Figure 4 shows the relationships between the creep strains and time of the PPy actuators driven in the electrolyte solutions with the different potential sweep rates. The time dependences look similar, which possibly suggests that the creep strain of the PPy actuators mostly depend on time but not on the potential sweep rate. This may mean that the PPy films swell both in the water and 2-propanol water solutions, and that the swelling of the PPy is larger in the 2-propanol electrolyte solution. This situation is more clearly described in Figure 5. Figure 5 shows the potential sweep rate dependence of the creep strain measured at the time of 1000 s. The creep strains are mostly determined by the time under the 0.3 MPa stress.

Figure 6 shows the potential sweep rate dependences of electrochemical strain rate of the PPy actuator in the electrolyte solution containing 0 and 20% of 2-propanol. The electrochemical strain evidently is independent of the potential sweep rate, and those for the electrolyte solution with 20% 2-propanol are always

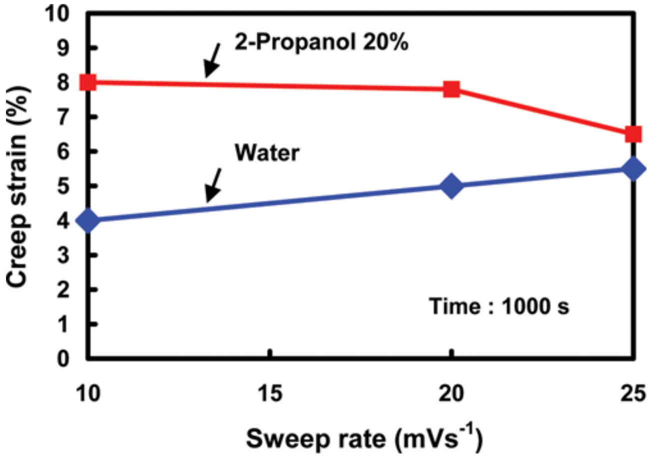

Figure 5. Sweep rate dependences of creep strains for PPy actuators in LiTFSI solutions with 2-propanol concentrations of 0 (water) and 20%.

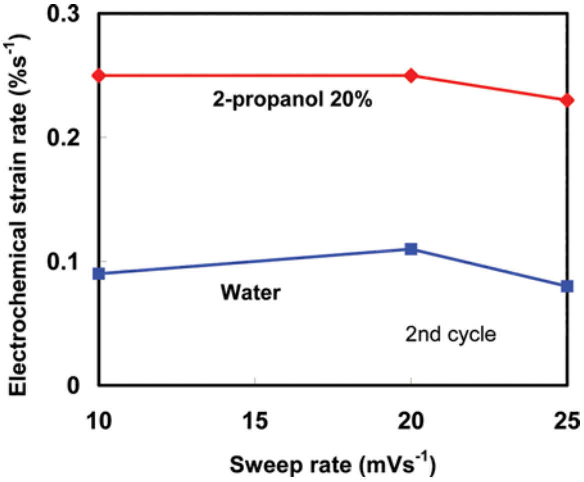

Figure 6. Sweep rate dependences of electrochemical strain rates for PPy actuators in LiTFSI solutions with 2-propanol concentrations of 0 (water) and 20%.

larger than those for the electrolyte solution with 0% 2-propanol. If the ionic flow rate in the electrolyte solution influences the electrochemical strain, the electrochemical strain rate should be dependent on the potential sweep rate. This is because the potential sweep rate should modify the ionic flow rate in the electrolyte solution. Since this is not the case, another mechanism should be considered in the PPy actuator functions. Hara *et al.* reported that their TFSI-doped PPy actuators exhibited the maximum deformation when their aqueous LiTFSI electrolyte solution contains 20 to 40% of propylene carbonate [12]. They pointed out that these phenomena were due to the swelling of the PPy film with propylene carbonate. The PPy film was reported to have porous and sponge like structures, and the swelling of the film increased the porous spacing. This will make the anions more easily penetrate into the PPy film, which resulted in the increase of the deformation of the PPy actuators.

It is speculated that the surface tension and viscosity of water and 2-propanol may influence the electrochemical deformation of the PPy actuators. Table 1 compares the surface tension and viscosity of pure water and 2-propanol for 20°C. The data were taken from the web page of National Institute of Standards and Technology (NIST). The surface tension of 2-propanol is 21.7 dyn $\cdot$ cm^{-1} that is nearly 30% of that of water. Therefore, when the PPy actuator is positively biased, TFSI^{-}

Table 1. Comparison of surface tension and viscocity for water and 2-propanol at 20°C (data taken from the web page of the National Institute of Standards and Technology (http://webbook.nist.gov/chemistry/fluid/)

	Surface tension (dyn $\cdot$ cm^{-1})	Viscosity (mPa $\cdot$ s)
Water	72.8	1.01
2-propanol	21.7	2.37

anions along with 2-propanol molecules might more easily penetrate into the porous structure of PPy. Thus, the increased deformation was observed for the 2-propanol concentration of 20%. The $TFSI^-$ ions diffused into the PPy porous structure in the positive potential region could be disturbed to escape from the PPy structures due to its high viscosity nature in the negative potential region.

The mechanisms for these behaviours still need to be more carefully investigated. However, the introduction of optimised amounts of 2-propanol into the LiTFSI electrolyte solution significantly improves the electrochemical strain of the PPy actuators.

4. Conclusion

The influences of the potential sweep rate on electrochemical and creep strains PPy actuators in aqueous LiTFSI electrolyte solutions with 2-propanol concentrations of 0 and 20% were compared under the load stress of 0.3 MPa. The electrochemical strain rates in the 0 and 20% 2-propanol solution were found to be approximately $0.1\%\,s^{-1}$ and $0.25\%\,s^{-1}$, respectively, and they are nearly independent of the sweep rate between 10 and $25\,mV\,s^{-1}$. These results suggest that the TFSI anion penetration into the PPy films might be limited by the interactions between the electrolyte and the PPy surface, and the reduced viscosity in the LiTFSI electrolyte solution containing 2-propanol possibly enhances the doping and dedoping of TFST anions along with the swelling effect of the PPy film by 2-propanol. The creep rate was more rapidly increased as time elapsed in the electrolyte solution containing 20% 2-propanol, which was due to the swelling of PPy film in the electrolyte.

Acknowledgment

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