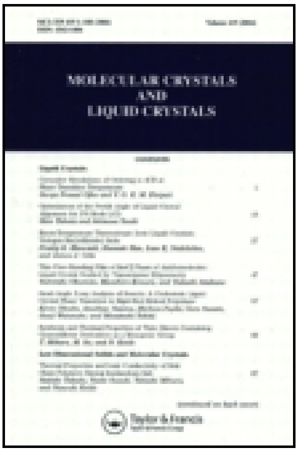

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Influence of Electrochemical Actuations on Mechanical Properties of PPy Actuators in Electrolyte Solutions Mixed with 2-propanol or Methanol

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Changes in Young's modulus, tensile strength, and tensile strain at break of polypyrrole (PPy) actuators after electrochemical actuations were investigated. The actuators made of 150 μm-thick PPy films with an area of 5 × 20 mm^2 were fabricated using electropolymerization. The actuators were functioned in aqueous lithium bis(trifluoromethansulfonyl)imide (LiTFSI) electrolyte solutions containing 0% or 20% of 2-propanol or methanol. Actuating strains of the actuators functioned in the electrolyte solutions containing 2-propanol or methanol were larger than the electrochemical strain of the actuator functioned in the electrolyte solution without 2-propanol or methanol. However, notable increase in the Young's modulus and reduction in the tensile strength and the tensile strains at break were observed after actuations in the electrolyte solution containing 0% or 20% of 2-propanol or methanol.

Keywords Soft actuators; polypyrrole; Young's modulus; tensile strength; methanol; 2-propanol

1. Introduction

In recent years, soft actuators consisting of conductive polymers such as polypyrrole (PPy) have been extensively studied and reported [1–3]. A PPy actuator expands and contracts by doping and dedoping ions under potential voltages in an electrolyte solution. PPy soft actuators have extremely large strains up to 40% and large stresses up to 1 MPa [3]. Therefore, PPy actuators may be suitable for some kinds of micro actuators used in microelectromechanical systems (MEMS) [5]. Some previous papers described increased PPy actuating strain by functioning PPy actuators in electrolyte solutions mixed with propylene carbonate [6] or 2-propanol [7]. However, the PPy actuators in these electrolyte solutions showed swelling (electrochemical creep) after repeated actuation processes under stress. In addition, the PPy films seemed to be more fragile after repeated actuations. Thus, it may be

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important to measure stress-strain characteristics before and after the repeated actuations. Some previous papers reported on measurements of the stress-strain characteristics of PPy films [8,9]. However, no paper reported on the change of the mechanical characteristics after repeated actuations to the best of our knowledge.

In this paper, we report on comparisons of actuating strain and electrochemical creep of PPy films during actuations in aqueous electrolyte solutions containing or not containing 2-propanol and methanol. The changes of stress-strain characteristics of these PPy actuators before and after the repeated actuations in these electrolyte solutions are also reported.

2. Experimental Procedure

The deposition 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 $mAcm^{-2}$ 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 strips to form the PPy actuators with the dimension of 20 × 5 mm^2

The PPy actuator was used as the working electrode in the 1 M LiTFSI aqueous electrolyte solutions containing 0% or 20% of 2-propanol or methanol to study the influences of electrochemical actuations on the changes of mechanical characteristics of the PPy actuators in different electrolyte solutions. The concentration of 2-propanol was selected to be 20% since the maximum actuating strain was confirmed at the 2-propanol concentration [7]. The concentration of the methanol was tentatively determined because no extensive research on the concentration dependence of the actuation behaviors was completed. 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 peak values of the potential voltage were -1 and +1 V, and the potential sweep rates were 10 mVs^{-1}. A load stress of 0.3 MPa was applied on the PPy actuators by placing a corresponding weight. The extension and contraction of the PPy actuator were measured by monitoring the displacement of the weight position using a laser displacement sensor as described in the previous publications [3–5,7].

The measurements of stress-strain characteristics of the PPy films were made using a tensile/compression testing machine (Imada, SV-52). The PPy films were washed in deionized water and dried in air after actuations in the electrolyte solutions. Then, the tensile tests for these PPy films were performed in air. The tensile speed was 0.5 mms^{-1} for the 20 mm-long PPy films, and it corresponds to the strain rate of 2.5%s^{-1}.

3. Results and Discussion

Figure 1 shows the comparison of the strains as a function of time under the repeated potential voltage sweeps between −1 and 1 V at 10 mVs^{-1} up to ten cycles. Here, an actuating strain was defined as a difference between the bottom of strain and the peak of

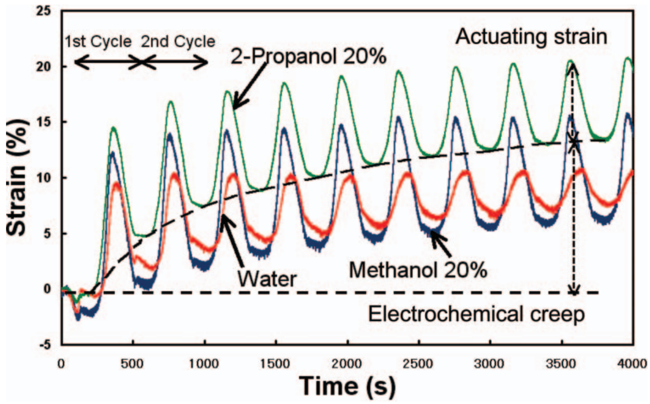

Figure 1. Strains of PPy actuators in LiTFSI solutions with or without 20% of methanol and 2-propanol.

strain as shown in Fig. 2. On the other hand, an electrochemical creep was defined at the strain background change as shown in the difference between the dotted lines.

The actuator in the aqueous electrolyte solution without 2-propanol or methanol (water) exhibited an actuating strain of 10 % at the first cycle, and the actuating strain rapidly decreased to 3% after 10 cycles of the actuations. The electrochemical creep of the actuator functioned in the electrolyte solution without 2-propanol or methanol (water) increased to 8% after 10 cycles. The actuator in the electrolyte solution with 2-propanol exhibited an increased actuating strain of approximately 12 % at the first cycle, and the electrochemical strain decreased to 8% after 10 cycles of actuations. On the other hand, the actuator in the electrolyte solution with methanol exhibited an increased actuating strain of 13 % at the first cycle, and the actuating strain decreased to 10% after 10 cycles of actuations. The electrochemical creep of the actuator functioned in the methanol solution was 6% after 10 cycles. Thus, it can be concluded that the PPy actuator functioned in the electrolyte solution containing 20% of methanol had larger actuating strain of 10% and the smaller electrochemical creep after 10 cycle actuations compared to the actuators functioned in the electrolyte solutions containing 0% (water) or 20% 2-propanol.

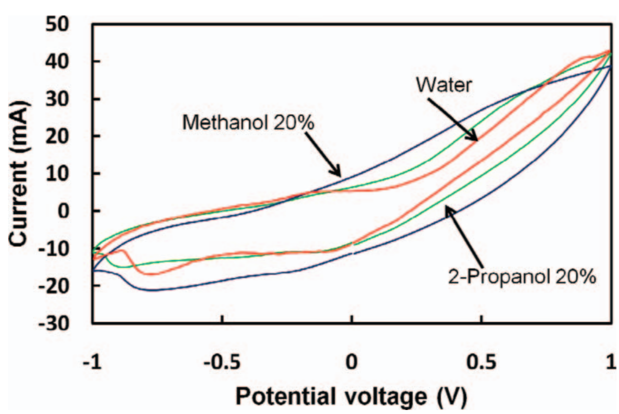

Figure 2. Cyclic voltammograms of the PPy actuators functioned in each LiTFSI solutions.

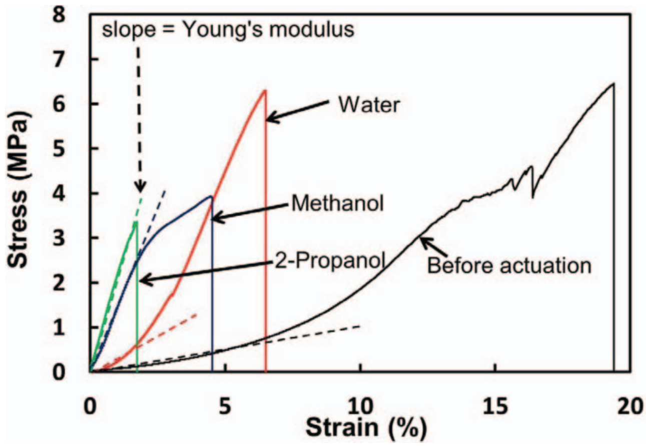

Figure 3. Strain-stress characteristics of PPy actuators functioned in LiTFSI solutions with or without 20% of 2-propanol or methanol.

Figure 2 shows the corresponding cyclic voltammograms (CV) of the PPy actuators measured during the 2nd cycle. After the repeated actuation up to 10th cycles, the CV characteristics remained similar. The larger hysteresis of the PPy actuators driven in the electrolyte solutions with methanol or 2-propanol implicates the enhancement of the $TFSI^-$ ionic motions into or outwards the PPy actuator, which explains the larger actuating strains of the PPy.

The reason for the increased electrochemical strain of the PPy films actuated in the aqueous LiTFSI solutions containing 2-propanol or methanol have not been well clarified yet. Some previous publications suggested that these effects could be owing to swelling of the PPy films [6] or change of viscosity of surface tension or the electrolyte solutions [7].

Figure 3 shows the measured strain-stress characteristics of the PPy actuator films before actuation and after 10 cycles of actuations by the potential sweeps in the LiTFSI solutions containing 0% (water), 20% of methanol, and 20% of 2-propanol. The tensile strain rate was 2.5% s^{-1}. The tensile testing was continued until the PPy films reached the tensile strains at break. The PPy film before actuations showed a slow initial increase of stress with the strain, and reached to a strain at break around 19%. The maximum stress at the break was defined as the tensile strength. The stress-strain curves for the PPy films after the 10 cycles of in the electrolyte water solution, 20% 2-propanol solution, and 20% methanol solutions showed the reduced tensile strength and the reduced strains at break. In addition, the initial slopes of the stress that correspond to Young's moduli became larger for the films after these actuations. Table I shows comparisons of the initial Young's modulus, the tensile strength, and the tensile strain at break of the PPy films before and after actuations in the electrolyte water solution, the electrolyte solution containing 20% methanol, and 20% 2-propanol. Notable increase in the Young's modulus from 0.13 GPa to 0.45 GPa and reduction in the tensile strains from 19% to 10% at break were observed after 10 cycles of actuations in the electrolyte solution without methanol or 2-propanol. These effects were more pronounced when the PPy actuators were functioned in the LiTFSI electrolyte solutions containing 2-propanol and methanol. For example, notable reduction in the tensile strength and the strains at break of the PPy films actuated in the electrolyte solutions containing 2-propanol or methanol were also observed. The PPy film actuated in the 20% 2-propanol solution showed the tensile strain at break of nearly 2.0%, while in the case of the methanol solution the reduced tensile strain at break was 4.5%. Although the

Table 1. Comparison of Young's modulus, tensile strength, and tensile strain before and after 10 cycles actuations in the aqueous electrolyte (LiTFSI) solution, the electrolyte solution containing 20% of methanol, and the electrolyte solution containing 20% of 2-propanol.

	Initial Young's modulus (GPa)	Tensile strength (MPa)	Tensile strain at break (%)
Before actuation	0.13	6.5	19
Aqueous solution	0.45	6.4	6.5
20% methanol	4.15	3.8	4.5
20% 2-propanol	4.3	3.4	2.0

introduction of methanol or 2-propanol in the LiTFSI electrolyte solutions improves the actuating strain of the PPy actuators, the degradation of the mechanical strength of the PPy films need to be considered when the films are used in actual product applications.

4. Conclusion

Changes in Young's modulus, tensile strength, and tensile strain at break of polypyrrole (PPy) actuators after actuations in electrolyte solutions were investigated. The actuators made of 150 μm-thick PPy films with an area of 5 $\times$ 20 mm^2 were fabricated using electropolymerization. The actuators were functioned in aqueous lithium bis(trifluoromethansulfonyl)imide (LiTFSI) electrolyte solutions containing 0% or 20% of 2-propanol or methanol. Actuating strains of the actuators in the electrolyte solutions containing 2-propanol or methanol were larger than the electrochemical strain of the actuator in the electrolyte solution without 2-propanol or methanol. However, notable increase in the Young's modulus and reduction in the tensile strength and the tensile strains at break were observed after actuations in the electrolyte solution containing 20% of 2-propanol or methanol.

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