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Fabrication of Anisotropic Polypyrrole Actuators

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Abstract: The novel features of electrochemical actuators fabricated from a cylindrical polypyrrole (PPy) pipe prepared by the electrochemical polymerization techniques have been described. This cylindrical PPy pipe was cut into a rectangular film and its electrochemical and electrical properties were measured. When the inner surface of the PPy film (surface in contact with electrolyte when PPy was polymerized) was insulated and redox was carried out, the PPy film bent toward the outer surface (surface in contact with a slender Teflon pipe when PPy was polymerized) upon reduction and returned to its original shape upon oxidation. However, the bending was not completely accompanied by redox when the outer wall side of the PPy film was insulated. Although such an anomalous bending in the PPy film actuator cannot be explained satisfactorily at this stage, we speculate that the bending phenomena are due to steric effects from cation insertion and extraction.

Keywords: *Electrochemical polymerization, Polypyrrole and derivatives, Mechanical tools and devices*

1. INTRODUCTION

By anodizing aromatic compounds such as pyrrole and thiophene, polymers of aromatic compound comes out on a surface of electrode and it is widely used synthesis of conducting polymers as

an electrochemical polymerization technique. Upon electrochemical polymerization, the electrode surface is coated with a uniform film and films were prepared with extremely ease. But the growth of powdered and fractal forms has been observed at times. Conducting polymers with highly conjugated π -electron system have been of extensive interest as a new type of electronic conductor ever since the discovery that these polymers could be oxidized or reduced over the full range from insulator to metal. Proposals of various applications of conducting polymers such as secondary battery, sensors, etc., have also stimulated synthesis of new conducting polymers. These polymers can be driven reversibly between the conducting and insulating states through electrochemical charge-discharge processes in an electrolyte solution or through chemical redox in a solution or in a gaseous atmosphere.

On the other hand, the volume change of conducting polymer gels due to charging-discharging, etc. has also been suggested for actuator and sensor uses. Conformational changes and simultaneous shrinking or swelling in response to external stimulus such as temperature change or electrical charge have been observed in various synthetic polymer gels, several other properties such as optical, magnetic, electrochemical activity of conducting polymers are also modified during the redox and a large number of applications such as for conducting

polymers has been proposed

We have been trying to prepare fibrous conducting polymers using an electrochemical polymerization technique. In this paper, the novel features of electrochemical actuators fabricated using polypyrrole films are described. That is, as a result of investigating the redox process of cylindrical PPy fibers, they have a function as an actuator and novel behavior was observed in their motion properties.

II. EXPERIMENTAL

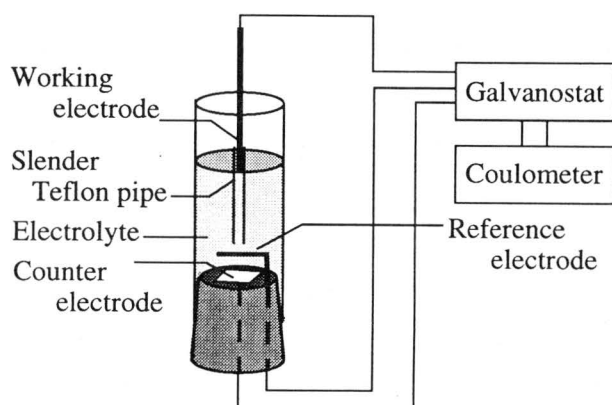


Fig. 1. Schematic diagram of an equipment of electrochemical polymerization.

Figure 1 shows an electrochemical cell for preparing the cylindrical PPy pipe containing an aqueous solution of *p*-toluenesulfonic acid sodium salt (*p*-TSNa, 1mol/l) with a Ni plate auxiliary electrode and an Ag reference. The working electrode was a Ni wire of about 0.2 mm diameter in pyrrole (1mol/l) and a slender pipe made of poly(terafluoroethylene), Teflon, of about 1 mm inside diameter was attached on top of the Ni wire. This working electrode was used to electrochemically polymerize cylindrical PPy pipes in the aqueous solution. This electrochemical cell was set up in a constant temperature bath and a constant cur-

rent of 0.14 mA was applied between the working electrode and the counter electrode.

III. RESULTS AND DISCUSSION [1,2]

By constant current flow, PPy was deposited on top of the Ni wire (working electrode), grew fractal-like along the transverse direction on the surface of electrolyte solution, and arrived at the inner wall of the slender pipe. Then, PPy grew continuously along the inner wall of a teflon pipe.

Figure 2 shows a cross sectioned photograph of the PPy fiber taken by SEM (JEOL. JSM-6100). The PPy fiber obtained was relatively flexible; uniform and cylindrical PPy fibers with an outside diameter of 1mm and a thickness of about 10 μ m were synthesized.

The conductivity of cylindrical PPy fiber showed marked anisotropy. PPy is readily produced by electrochemical procedures and is attractive because of its good environmental stability and relatively high electrical conductivity. The conductivity of growth direction is about 100S/cm and larger by about 5 orders of magnitude than that of the direction of thickness. It is suggested that the main chain of PPy fiber orients to the direction of growth.

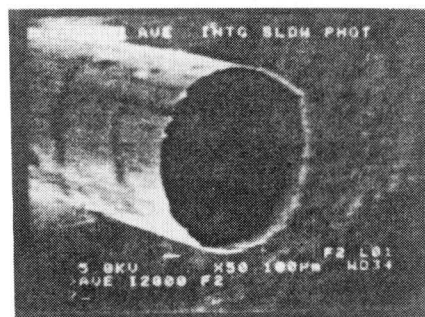


Fig. 2. SEM image of a section of polypyrrole fiber.

The bending phenomena were observed during the redox process of Ppy strip. That is, the PPy

fiber bends in the direction of the surface in contact with Teflon during the electrochemical undoping process and is restored to its original position upon doping.

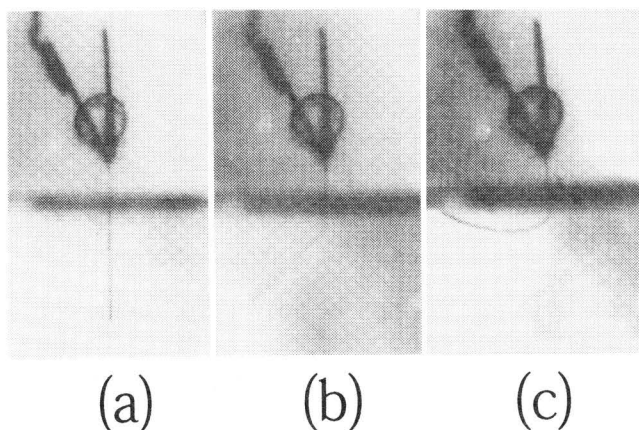


Fig. 3. Photographs of bending of the cylindrical polypyrrole-fiber actuator. (a) doped state, (b) intermediate state, and (c) undoped state

Electromechanical actuators using conducting polymers have been proposed by Baughman *et al.* Otero *et al.* demonstrated an actuator utilizing electrochemical reduction of oxidized PPy. An interesting chemomechanical motion of polymer gel in the presence of a surfactant electrolyte under an applied electric field has been demonstrated by Osada *et al.* However, in our experiment, the novel behavior was observed as follows. If the inner wall side (contacting surface with electrolyte when PPy was polymerized) was insulated and the redox was carried out, the PPy fiber bends toward the outer wall side (contacting surface with when PPy was polymerized). However, the bending phenomena of PPy fiber were not completely observed when the outer wall side was insulated. As an example, figure 3 shows photographs of motion of the PPy-fiber actuator observed in aqueous solution containing 1 mol/l *p*-TSNa. Fig 3 (a) shows a behavior when 0.85 V (vs. Ag/Ag⁺) was

applied to oxidize the PPy fiber, Fig 3 (c) a behavior when -0.85 V (vs. Ag/Ag⁺) was applied to reduce the PPy fiber, and Fig 3 (b) a behavior of along motion. These cycles were reversible for about 50 cycles without any indication of degradation. The response time from (a) state to (c) state is about 1 second. However, the displacement from (c) state to (a) was required several seconds.

We speculate the bending of the PPy fiber actuator during redox in an aqueous solution containing *p*-TSNa is due to the volume change arising from dopant insertion or extraction. However, it is not clarified whether *p*-TS⁻ or Na⁺ does play a key role. We have attempted to use TEAp-TS and SPSNa other than *p*-TSNa as supporting salts in driving electrolytes. Figure 4 shows the cyclic voltammograms in 1.0 mol/l *p*-TSNa, TEAp-TS and SPSNa aqueous solutions. All were measured at the sweep rate 15 mV/s. In SPSNa solution, both the oxidation/reduction current and the bending of the PPy fiber actuator were clearly observed, and its current peak potential coincided nearly with that in *p*-TSNa solution. On the other hand, in TEAp-TS solution, neither the oxidation/reduction current nor the bending were observed. These results indicate the possibility of either SPS⁻ or Na⁺ transport into and out of the PPy fiber actuator. However, it must be impossible for SPS⁻ to get into the PPy, because it is polymeric ion. Therefore, it is most likely that the insertion and extraction of Na⁺ play a key role in the bending. The coincidence of peak potentials between *p*-TSNa and SPSNa in the cyclic voltammogram also supports this mechanism.

Figure 5 shows the concentration dependence of the arrival time with various supporting salts having Na⁺ as cation. The arrival time is time required for the PPy fiber actuator to bend and arrive at the

surface of the electrolyte solution when the potential was changed stepwise from 0.2 V vs. Ag/Ag⁺ to -0.85 V vs. Ag/Ag⁺. The horizontal axis was plotted in a log scale of electrolyte concentration. Obviously, the behavior does not depend on the anion, indicating that Na⁺ only contributes to the bending. The PPy fiber actuator could not bend enough to arrive at the surface in 3.0mol/l SPSNa solution, because the bending was disturbed by high viscosity of the concentrated SPSNa solution.

The bending of the PPy fiber actuator in electrolyte solutions with Na⁺ could be observed, while it could not be observed in TEAp-TS solution. This indicates that the size of cation influences in the bending. Therefore we compared the motion properties of the PPy fiber actuator in electrolyte solutions with the various sizes of cation. *p*-TSNa, *p*-TSPy, TMA *p*-TS, TEA *p*-TS and TBA *p*-TS were used as supporting salts. The approximate ionic radii of cations composing each electrolytes are as follows. Na⁺ : 0.95 Å, Py⁺ : 2.2, TMA⁺ : 2.5 Å, TEA⁺ : 3.6 Å and TBA⁺ : 7.6 Å.

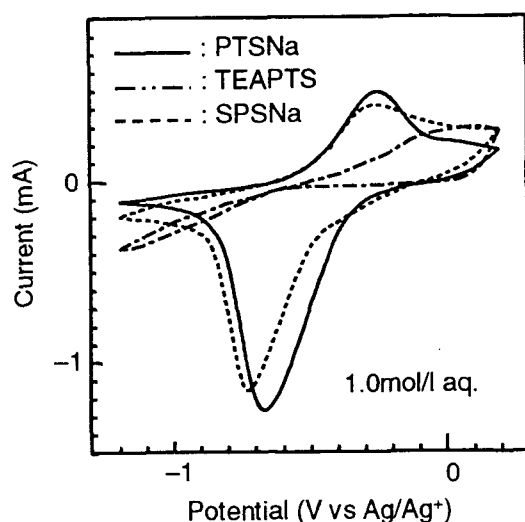


Fig. 4. Cyclic voltammograms of PPy fiber actuator in aqueous solutions of 1.0 mol/l *p*-TSNa, TEAp-TS and SPSNa.

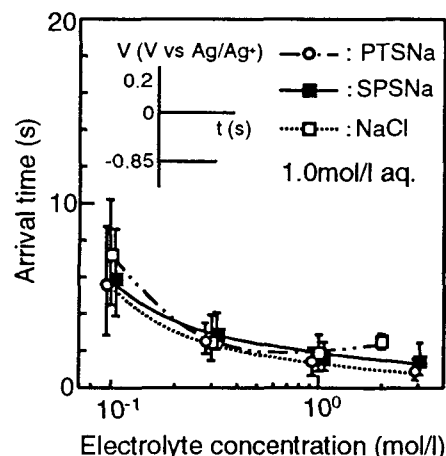


Fig. 5. Dependence of the arrival time on the concentration of various supporting salts (*p*-TSNa, SPSNa and NaCl) in the driving electrolyte.

IV. CONCLUSION

Such an anomalous bending in PPy fiber actuator cannot be explained satisfactorily at this stage. However, as a tentative explanation, we suggest that the bending phenomena are due to steric effects from cation insertion and extraction.

Such behavior based on the electrochemical stimulus gives some information connected with ionic transfer and storage and as an electrochemical actuator which directly converts the electrical energy into the mechanical energy it suggests that the cylindrical PPy fiber can be put to practical use.

Acknowledgment

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