Highly Stretchable and Powerful Polypyrrole Linear Actuators

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A polypyrrole (PPy) film, prepared electrochemically from methyl benzoate solution of tetra-*n*-butylammonium tetrafluoroborate on Ti electrode, showed 12.4% strain and 22 MPa stress induced electrochemically in $NaPF_6$ aqueous solution. The large strain and stress may be due to doping-dedoping of anion and a conformational change of PPy chains.

Conducting polymers, such as polypyrrole (PPy), polythiophene and polyaniline, are promising soft actuators potentially applicable to artificial muscles because of their large stress (from 3 to 5 MPa)[1–4] driven electrochemically, 10 times more than mammalian skeletal muscles (0.35 MPa).[5] The applications of conducting linear actuators have been, however, quite limited owing to their moderate electrochemical strain (up to 3%)[1,2,6] that makes mechanisms of actuators complicated. Development of highly stretchable conducting polymer actuators is, therefore, a challenging and urgent subject especially for the robotic industry where relatively huge and heavy motors have to be used.

We have tackled to prepare electrochemically a number of PPy films and to measure their performance for a linear actuator, and finally found a series of PPy films exhibiting more than 10% expansion-contraction ratio for one redox cycle. Moreover, these PPy films also showed large stress driven electrochemically. Here, the electrochemical contraction of PPy films produced force, that is, PPy films pulled up a load when they contracted together with dedoping. Accordingly, we will focus mainly on the electrochemical strain and stress of PPy films in this paper.

Polypyrrole films were galvanostatically ($0.2\,mA\,cm^{-2}$) synthesized on Ti, Ni, or indium tin oxide (ITO) electrode for 4 h from $0.25\,mol\,dm^{-3}$ pyrrole and $0.5\,mol\,dm^{-3}$ tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$) in organic solvents such as methyl benzoate at room temperature. The films obtained (thickness: ca. 0.02 mm, conductivity: $80–120\,S\,cm^{-1}$) were peeled off and rinsed with acetone, then cut into a 15-mm length × 2-mm width strip and set in a glass cell with a pin hole at the bottom as described elsewhere[7] to measure change in length of the films by using a laser displacement meter (KEYENCE LC-2400). The definition of expansion-contraction ratio in this work is change in length of a strip divided by an original strip length ($\Delta l/l_0$) when potential is applied between −0.9 and +0.7 V vs Ag/Ag^+ by using a potentiostat/galvanostat (Princeton Applied Research Model 263A). The load for the sample was typically ca. 0.1 MPa for measuring the maximum electrochemical strain, and increased until the film was broken. Here, the PPy film showed the maximum electrochemical stress.

Figure 1 shows an anion driven electrochemical stretching of a PPy film, prepared from methyl benzoate solution of $TBABF_4$ on Ti electrode at room temperature, in $NaPF_6$ aqueous solution ($1.0\,mol\,dm^{-3}$) cycled between −0.9 and +0.7 V vs Ag/Ag^+ at room temperature. When the potential was swept to the cathodic direction at $2\,mV\,s^{-1}$, the PPy film contracted by 4.8% with dedoping. The sweep was then turned to the anodic direction, the PPy film lengthened with doping. Rapid elongation of the film started dramatically at +0.3 V vs Ag/Ag^+ when an anodic peak appeared on a cyclic voltammogram (CV), as shown in Figure 1. Note that the redox peak at −0.65 V/−0.45 V was not related to the PPy redox but to a redox of $NaPF_6$ on Pt, which was used for holding the PPy strip. The total expansion-contraction ratio ($\Delta l/l_0$) for one redox cycle was 12.4%, much larger than those of other conducting polymer actuators. The expansion-contraction ratio decreased slightly to 10.8% probably because the packing of PPy chains did not revert to the original form after the redox cycle with doping and dedoping. The third and the following CV and expansion-contraction cycles were similar to those in the second cycle. The maximum expansion-contraction ratio achieved so far was 15.1% when a PPy film was prepared on Ni from $TBABF_4$ butyl benzoate solution.

Common organic solvents used for the electrochemical polymerization of pyrrole such as propylene carbonate and acetonitrile were classified as the second best group, showing 8–

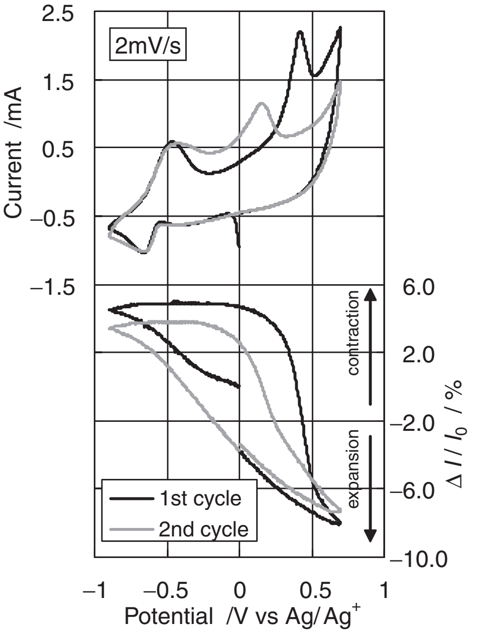

Figure 1. A CV and an electrochemical stretching of a PPy film prepared from methyl benzoate solution of $TBABF_4$, cycled in $NaPF_6$ aq.

10% of expansion-contraction ratio even if $TBABF_4$ was employed as an electrolyte. Water was not a suitable solvent for this system although water has been often used for the electropolymerization of pyrrole. An aqueous solution of $NaBF_4$, for instance, gave a brittle PPy film showing 0.3% strain.

The expansion-contraction ratio of PPy films prepared from methyl benzoate solution of $TBABF_4$ did not depend very much on the electrode used for the electropolymerization, but PPy films prepared on ITO was inclined to stretch faster than those prepared on metal electrodes. When the scan rate was set at $10\,mV\,s^{-1}$, PPy films prepared on metal electrodes tended not to exhibit their maximum performance of electrochemical stretching so that the scan rate was set at $2\,mV\,s^{-1}$, as shown in Figure 1, probably because metal electrodes gave more compact PPy films.

Mechanisms of the large electrochemical stretching of the PPy films may be due to doping-dedoping of anion together with a conformational change of PPy chains.[8] Volume change of PPy films caused by doping-dedoping should be the same if the dopant used is the same, so such a large stretching seems to result mainly from the conformational change of PPy chains induced by doping and dedoping.

The expansion-contraction ratio varied with anions for measuring the electrochemical stretching.[9] The order for the highly stretchable PPy actuators was also

$$PF_6^- > BF_4^- > Cl^-,$$

due presumably to the anion size.

In general, as the load became heavier, the electrochemical stretching of PPy films became smaller. As shown in Figure 2, the maximum electrochemical stress obtained just before breakage of PPy films was 22 MPa for a PPy film prepared from methyl benzoate solution of $TBABF_4$ on Ti, where the expansion-contraction ratio was 1.0%. It should be noted that mechanical tensile strength of the film was more than 80 MPa. At a fairly heavy load equivalent to 5 MPa, the film still maintained 7% strain. The large electrochemical strain and stress of the PPy film make conducting polymers fit for practical use as a linear soft actuator.

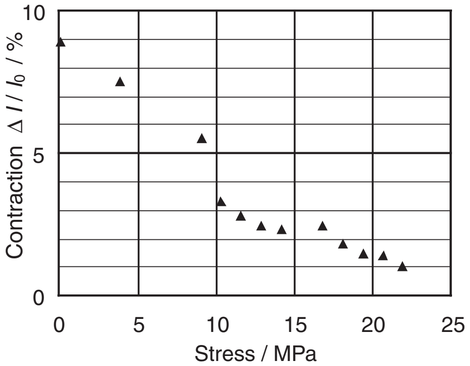

Figure 2. Correlation between electrically induced stress and contraction of a PPy film cycled between −0.9 and +0.7 V vs Ag/Ag^+ at $10\,mV\,s^{-1}$ in $NaPF_6$ aq.

The electrochemical stress strongly depended on electrolytes, solvents and electrodes used for the film preparation. $TBABF_4$ and tetra-*n*-butylammonium trifluoromethanesulfonate ($TBACF_3SO_3$) not only gave highly stretchable actuators but also powerful ones, whereas a PPy film prepared, for example, from sodium *p*-phenolsulfonate aqueous solution showed the maximum strain of 2.7% and the maximum stress of 3.5 MPa. When PPy films were prepared from methyl benzoate solution of $TBABF_4$, ITO and Ni electrodes also gave powerful actuators whose maximum stresses were more than 10 MPa. When 1,2-dimethoxyethane, which also gave highly stretchable PPy actuators with $TBABF_4$, was used as a solvent, PPy films obtained on ITO electrode showed a small stress (1.4 MPa), whereas metal electrodes gave powerful actuators (up to 14 MPa).

Of organic solvents giving highly stretchable PPy actuators, esters such as methyl benzoate which dissolve the electrolyte with difficulty solely gave powerful actuators whatever the electrode was used. When the electrolytic solution of $TBABF_4$ was prepared, an addition of pyrrole turned $TBABF_4$ soluble in methyl benzoate. It seems that some interaction between pyrrole and BF_4^- made the electrolyte soluble in the solvent, and the interaction remained even after the electropolymerization of pyrrole, giving densely packed PPy chains.

In addition, the electrochemical stress of PPy actuators described above had a positive correlation with the mechanical tensile strength of the films. These results might be attributable to the dense packing of PPy chains formed during the electropolymerization of pyrrole where an interaction between pyrrole and BF_4^- (or $CF_3SO_3^-$) existed.

The PPy films described in this work indicated much larger strains and stresses generated electrochemically than those of other conducting polymer actuators, and thus applications of conducting polymer actuators to the robotic industry have become realistic. We have already fabricated a variety of PPy actuators,[10] some of which were long enough to visually recognize linear actuation or powerful enough to pull up a 20-kg weight. Detail of our work will be available soon.

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