The Correlation between Electrically Induced Stress and Mechanical Tensile Strength of Polypyrrole Actuators

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Highly stretchable and powerful PPy film actuators, prepared electrochemically from a methyl benzoate solution of tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$), showed a positive correlation between the electrochemical stress and the mechanical tensile strength. The more flexible $CF_3SO_3^-$-doped PPy suits multi-wound or multi-folded actuators that can be used as artificial muscles.

Conducting polymers such as polypyrrole (PPy) and polyaniline expand and shrink with doping and dedoping, respectively, and therefore can be used as actuators.[1,2] The advantages of conducting polymer actuators over the conventional motors are as follows:

1. large stress (3–5 MPa) induced electrically,
2. light in weight,
3. low drive voltage (1–2 V),
4. silent movement.

Particularly the large stress, 10 times larger than that (0.35 MPa)[3] generated by mammalian skeletal muscles, has been considered as the most important property of the conducting polymer actuators for applications to robots, powered suits, artificial limbs, medical devices, and the replacement of conventional motors. The moderate strain (1–3%)[1,2,4] has, however, been restricting practical use of the conducting polymer actuators.

Recent breakthroughs[5] in both the electrochemical strain and stress of PPy actuators will enhance interest in conducting polymer actuators as artificial muscles. The next step to develop the PPy actuators for practical use would be how to fabricate actuator devices. It is of importance to use PPy actuators with a large strain and stress induced electrically, but their mechanical strength and flexibility should also be considered. PPy actuators doped with tetrafluoroborate (BF_4^-) or trifluoromethanesulfonate ($CF_3SO_3^-$) prepared on a Ti electrode from a methyl benzoate solution exhibited large strain (12–15%) and stress (20–22 MPa) generated electrically. The large electrochemical stress strongly depended on the mechanical tensile strength of the PPy actuators, whatever the electrodes and the solvents used for the electropolymerization of pyrrole. Of the electrodes used so far, the Ti electrode gave PPy films showing the largest electrochemical stress (22.0 MPa) and mechanical tensile strength (93.0 MPa), whereas indium tin oxide (ITO) electrode gave PPy films with smaller electrochemical stress (13.3 MPa) and mechanical tensile strength (39.4 MPa), but still considerably larger than those of the conventional conducting polymer actuators. PPy electrochemically deposited on Ti using $TBABF_4$ (or $TBACF_3SO_3$) and methyl benzoate as the electrolyte and the solvent, respectively, was a compact film having presumably long PPy chains. Strong interactions between the PPy chains could result in the large electrochemical stress and the mechanical tensile strength mentioned above. A similar correlation was also observed when 1,2-dimethoxyethane was used as the solvent for the PPy preparation, but both the electrochemical stress (14.2 MPa) and tensile strength (84.9 MPa) of PPy deposited on Ti were smaller than those prepared from the methyl benzoate solution.

Figure 1 illustrates the correlation between the electrically generated stress and the mechanical tensile strength of PPy prepared from a methyl benzoate or 1,2-dimethoxyethane solution of $TBABF_4$ on various electrodes. In both cases, metal electrodes gave PPy films exhibiting a large stress induced electrically and mechanical tensile strength. The positive correlation could be attributable to some physical properties of the PPy chains such as entanglement of the chains, interaction between the chains, etc., which may be common properties giving large electrochemical stress and mechanical tensile strength. It is therefore important for obtaining PPy actuators with a large electrochemical stress to prepare mechanically strong films. A suitable combination of the electrolyte and the solvent used in the PPy preparation could strengthen the interaction between PPy chains and also between the aromatic rings of PPy and dopant anions, producing compact and tough PPy films. In addition, mild conditions of the electrochemical polymerization such as a lower temperature and smaller current density improve the quality of PPy films. PPy films obtained at around 0 °C appeared to be smoother and more flexible than those prepared at room temperature. Further reduced temperatures such as −20 °C tended to give brittle films, presumably due to a lower ion conductivity of the electrolytic solution for the electropolymerization. It should be emphasized that the electrode used strongly depended on the electrochemical stress and mechani-

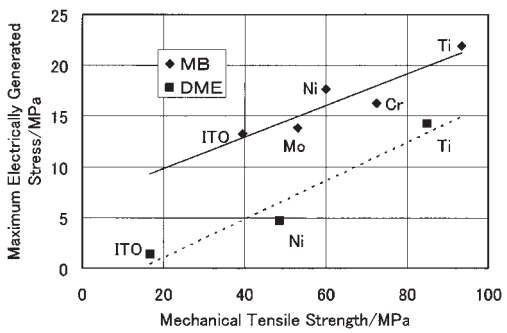

Fig. 1. Correlation between electrically generated stress and mechanical tensile strength of PPy films prepared from methyl benzoate (MB) or 1,2-dimethoxyethane (DME) solution of $TBABF_4$ on various electrodes.

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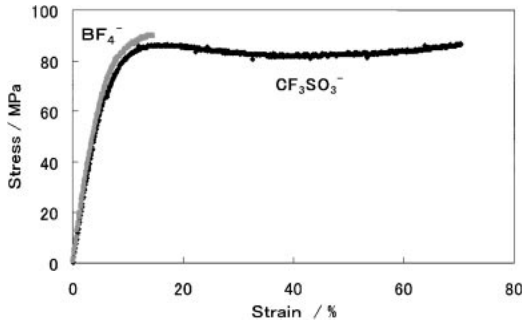

Fig. 2. A stress–strain diagram of PPy films prepared from methyl benzoate solution of $TBABF_4$ or $TBACF_3SO_3$ on Ti electrode.

cal tensile strength, but electrochemical strain (expansion–contraction ratio) was almost kept constant (11–15%) so long as $TBABF_4$ (or $TBACF_3SO_3$) was used as the electrolyte. Suitable solvents for the preparation of the PPy actuator were described elsewhere,[5] and aromatic esters were the best for obtaining PPy with a large strain and stress induced electrochemically as well as a high mechanical tensile strength. Note that the PPy films doped with BF_4^- or $CF_3SO_3^-$ can be used not only for highly stretchable and powerful actuators but for conductive high performance films. PPy films doped with PF_6^- exhibited 12.8% strain induced electrically, but had a mechanical strength of only 44–53 MPa, smaller than the PPy films doped with BF_4^- or $CF_3SO_3^-$.

Besides fundamental properties of the PPy actuators, such as electrically induced strain and stress, the mechanical tensile strength and flexibility of the PPy films should be good enough to fabricate devices. Only the $CF_3SO_3^-$-doped PPy films met the specifications, although their electrochemical stress (20.8 MPa) was slightly smaller than those of the BF_4^--doped PPy actuators.

Figure 2 shows a stress–strain diagram of PPy films prepared from a methyl benzoate solution of $TBABF_4$ or $TBACF_3SO_3$ on Ti. The PPy with $CF_3SO_3^-$ was elongated by 60–100% at a tensile rate of 6 mm min^{-1}, whereas the PPy with BF_4^- was cut between 10–20%, resulting presumably from a larger degree of polymerization of $CF_3SO_3^-$-doped PPy than that of the BF_4^--doped PPy, although it is impossible to determine the molecular weight of PPy. This difference in the mechanical properties of the PPy should be the main reason why the $CF_3SO_3^-$-doped PPy is not only a highly stretchable and powerful actuator but also a very flexible film, able to be easily wound or folded, whereas the BF_4^--doped PPy shows a larger strain and stress induced electrically, but is slightly rigid and brittle.

The electrochemical stress and mechanical tensile strength of PPy films prepared from the methyl benzoate solution of $TBACF_3SO_3$ also depended on the electrode used. PPy films prepared on Ni or ITO electrodes showed a smaller stress (17.5 MPa and 15.0 MPa, respectively) induced electrically than those of the BF_4^--doped PPy films described above, but their mechanical tensile strength (89.3 MPa and 65.5 MPa, respectively) was considerably large, such that the mechanical properties of the $CF_3SO_3^-$-doped PPy seem to be somehow different from those of the BF_4^--doped PPy.

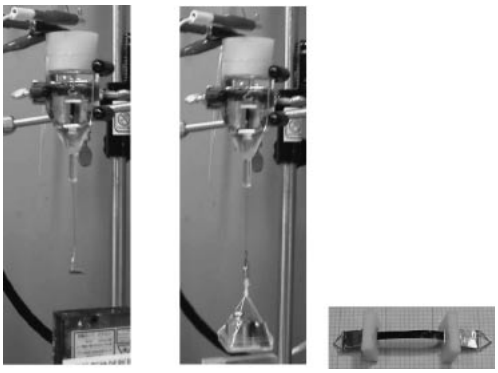

Fig. 3. Photographs of the apparatus for the measurement of electrochemical strain and stress of PPy actuators, and a PPy strip clamped with Pt and PTFE plates.

In conclusion, the highly stretchable and powerful PPy actuators, prepared from a methyl benzoate solution of $TBABF_4$, showed a positive correlation between the electrochemical stress and the mechanical tensile strength. The more flexible $CF_3SO_3^-$-doped PPy suits multi-wound or multi-folded actuators applicable to artificial muscles. The novel conducting polymer actuators based on PPy would be versatile artificial muscles applicable particularly where small space is available for the actuator devices.

Experimental

The electrochemical polymerization of pyrrole (0.25 mol dm^{-3}) was carried out galvanostatically (0.2 mA cm^{-2}) for 4 h with $TBABF_4$ or $TBACF_3SO_3$ (0.2 mol dm^{-3}) at 0 °C by using a Hokuto Denko HA-151 potentiostat–galvanostat. The PPy films obtained (thickness: ca. 0.02 mm) were cut into a 15-mm × 2-mm strip and set in a three-electrode glass cell with a pin hole at the bottom through which a tungsten wire passed to pull up a load (0.4 g), equivalent to 0.1 MPa, as shown in Fig. 3.

The electrochemical strain (expansion–contraction ratio) of PPy actuators was measured by using a laser displacement meter (KEYENCE LE-4000) when potential was applied to the PPy between −0.9 and +0.7 V vs Ag/Ag^+ at 2 mV s^{-1} in aqueous $NaPF_6$ solution by using a Princeton Applied Research Model 263A potentiostat–galvanostat. Details of the experimental conditions was described elsewhere.[5] The PPy strip (a free-standing film; ca. 0.005 g in weight) shown in Fig. 3 (left) pulled up an 80-fold heavier load than itself to measure the maximum electrochemical strain. In order to measure the maximum electrochemical stress, cycled between −0.9 and +0.7 V vs Ag/Ag^+ at 10 mV s^{-1}, the load suspended was increased up to 85 g shown in Fig. 3 (right), equivalent to 22 MPa. That is to say, the PPy pulled up a 17000-fold heavier load than the PPy itself.

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