Artificial Fibular Muscles with 20% Strain Based on Polypyrrole–Metal Coil Composites

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A fibrous polypyrrole Pt/Ir-coil composite actuator, prepared electrochemically from a methyl benzoate solution of tetra-*n*-butylammonium bis(trifluoromethylsulfonyl)imide (TBATFSI), exhibited 20% electrochemical strain in propylene carbonate/water solution of LiTFSI. The artificial muscle fibre based on TFSI-doped PPy–Pt/Ir coil composite has reached the same level of natural muscle's strain.

Conducting polymers (CPs) have been developed for more than a decade as artificial muscles, but little attention was paid due to their small strain (1–3%).[1–4] Recently, we have reported two CP actuators based on polypyrrole (PPy); a powerful type[5,6] and an extremely stretchable type.[7,8] The former was prepared electrochemically from a methyl benzoate (MB) solution of $TBABF_4$, $TBAPF_6$, or $TBACF_3SO_3$, exhibiting 13% strain and 49 MPa stress generated electrochemically. Of the electrolytes mentioned above, $TBACF_3SO_3$ gave a flexible and mechanically strong film such that actuator devices can be fabricated easily, and therefore PPy-$CF_3SO_3^-$ has been used for practical devices such as a diaphragm pump.[9] The latter was prepared similarly using bis(perfluoroalkylsulfonyl)imide, $(C_nF_{2n+1}SO_2)_2N^-$, as dopant, exhibiting 20–40% strain with moderate stress (2–10 MPa). As pointed out elsewhere,[10] there is a positive correlation between electrochemical stress and mechanical tensile strength of CP actuators, and the mechanical tensile strength of TFSI-doped PPy film was 36–38 MPa. The low mechanical strength might make it difficult to fabricate actuator devices.

Besides PPy actuator films, we have reported PPy–metal coil composite actuators as artificial fibular muscles,[11] one of the merits of which was to be used as "push" devices without complicated mechanisms.[11,12] Another merit should be the fact that PPy was protected by the metal framework. In case of PPy–metal coil composite actuators doped with $(C_nF_{2n+1}SO_2)_2N^-$ described in this paper, the second merit is significant to fabricate actuator devices because PPy films doped with $(C_nF_{2n+1}SO_2)_2N^-$ were spongy and soft. The fibrous PPy–metal coil composite actuator is robust and actuates massively with 20% strain as if it were a natural muscle fibre. A bundle of the PPy–metal coil composite bears a close resemblance to a skeletal muscle and such a biomimetic actuator device as an artificial fibular muscle is no longer considered a science fiction.

We have reported recently PPy films doped with TFSI actuated quickly in H_2O/propylene carbonate (PC) solution of LiTFSI because the PPy films swelled in H_2O/PC solution and large TFSI anions can transfer smoothly in the PPy film working as the dopant.[13] Therefore the fibrous PPy–metal coil composites doped with TFSI have become promising linear actuators with large deformation and fast response.

Preparation of PPy–metal coil composites was performed by electropolymerization similarly as described elsewhere[7,11] from an MB or dimethyl phthalate (MP) solution of TBATFSI (0.2 mol dm^{-3}) at 0.15 mA for 6 h at 0 °C on a Pt/Ir coil (diameter of the coil: 0.25 mm, diameter of the wire: 0.025 mm, the pitch: 0.050 mm, Ir content: 20%). Both PPy–Pt/Ir coil composite actuators had a rough PPy surface with large grains shown in Figure 1. The surface morphology was quite different from that of a PPy–W coil composite prepared with $TBABF_4$ as the electrolyte which had a compact and smooth surface.[11]

Figure 2 depicts a cyclic voltammogram (CV) and an electrochemomechanical deformation (ECMD) of a TFSI-doped

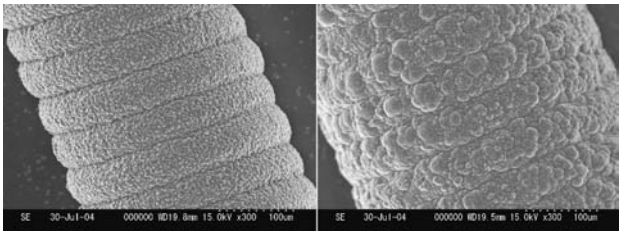

Figure 1. SEM photographs of PPy–Pt/Ir coil composite fibres prepared from an MB (left) and MP (right) solution of TBATFSI.

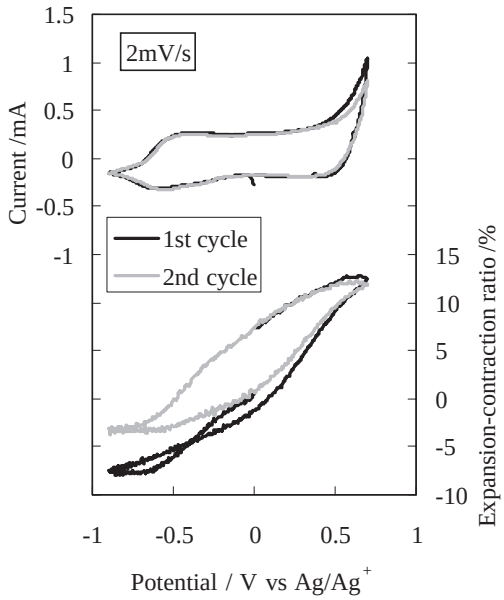

Figure 2. A CV and an ECMD of a TFSI-doped PPy–Pt/Ir coil composite actuator (16 mm) driven in H_2O/PC (60/40) solution of LiTFSI when potential was swept between −0.9 and +0.7 V vs Ag/Ag^+ at 2 mV s^{-1}.

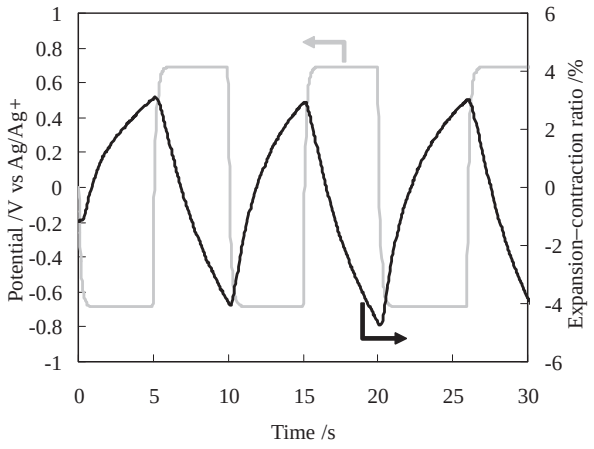

Figure 3. An ECMD of a TFSI-doped PPy–Pt/Ir coil composite actuator (13 mm) driven in H_2O/PC (60/40) solution of LiTFSI at ± 0.7 V vs Ag/Ag^+ (0.1 Hz).

PPy–Pt/Ir coil composite actuator (16 mm), cycled between -0.9 and $+0.7$ V vs Ag/Ag^+ at 2 mV s^{-1} at room temperature in H_2O/PC (60/40) solution of LiTFSI. One gram of load was applied for the measurement of ECMD. On applying the potential to -0.9 V, the PPy actuator contracted with dedoping of TFSI, and elongated dramatically on oxidation with doping. The electrochemical strain (the expansion–contraction ratio) for one redox cycle was 20.8%, much larger than that (11.6%) of BF_4^--doped PPy–W coil composite,[11] prepared similarly with $TBABF_4$ as the electrolyte, driven in aqueous $NaBF_4$ solution. The difference in the electrochemical strain mainly depended on the size of the dopants.

Figure 3 shows repeated electrochemical stretching of a TFSI-doped PPy–Pt/Ir coil composite actuator at ± 0.7 V vs Ag/Ag^+ at 0.1 Hz (square pulse) in H_2O/PC (60/40) solution of LiTFSI, driven by using a Hokuto Denko HA-151 potentio–galvanostat and a Wave Factory WF1946 multifunction synthesizer.[14] Stable and large electrochemical stretching (7.9% strain) was observed repeatedly. The electrochemical strain increased to 12% at 0.05 Hz. The visually recognizable ECMD should attract engineers who need linear actuators with large displacement and response rate.

The peak response rate obtained from Figure 3 was 6.6% s^{-1}, which was much faster than that (ca. 0.1% s^{-1}) of a BF_4^--doped PPy–W coil composite even though a large TFSI anion (ionic radius: 0.325 nm)[15] was applied for driving the PPy–Pt/Ir coil composite actuator. Such a large TFSI anion can go in and out of PPy easily, because PPy swelled in H_2O/PC (60/40) solution. A similar phenomenon was observed in a TFSI-doped PPy film driven in H_2O/PC (60/40) solution of LiTFSI.[13]

It should be noted that the peak response rate of 6.6% s^{-1} was smaller than that (up to 13% s^{-1}) of PF_6^--doped tubular actuators with Pt helical wire interconnects whose axial strain was up to 5%.[12] The large peak response rate was measured at ± 5 V. To our best knowledge, this was the highest response rate of CP actuators ever reported.[16] A tubular PPy-TFSI without any compliant metal electrode, prepared electrochemically from an MP solution of TBATFSI, exhibited a peak strain rate of ca. 8% s^{-1} such that the Pt/Ir coil not only decrease the voltage drop along the actuator to increase the response rate but also disturbed the actuation to decrease it. Therefore, more appropriate configurations of the metal coil are required. Preliminary experiments suggest that appropriate configurations of the metal coil and the zigzag-metal wire[17] for PPy-TFSI should be completely different from those for PPy-$CF_3SO_3^-$, a much more powerful actuator.[6]

Practically, linear CP actuators are required both high response rate and large displacement. The TFSI-doped PPy–Pt/Ir coil composite actuator exhibited 20.8% maximum strain with a response rate of 6.6% s^{-1}, and therefore suitable for fabricating practical artificial muscle fibre devices. The large electrochemical strain has reached almost the same level as that (20–40%)[18] of natural muscles although the response rate of muscle is still much higher (>100% s^{-1}).[12,18] Practical devices by the use of the TFSI-doped PPy-metal coil composite actuators are being fabricated. It has been found that micro-actuators for MEMS were most suitable applications.[19]

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