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Artificial Muscles Based on Polypyrrole Films -Morphology Control for Enhancement of Actuation-

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Recently, organic materials for electronics devices are attracted, because of their variety of functions such as light emitting, photovoltaic effect and switching due field effects in dry electronics devices. Wet devices like rechargeable batteries, dye sensitized solar cells, electro chromic and soft actuators are also interested in. We know that the performances of these devices strongly depend on not only the chemical structure of materials but also their arrangement of molecules (secondary structure or morphology). It should be noted that the higher performance is attained by well alignment or ordered assemble of molecules as well as the surface morphology.

In electrochemical process, the rate of reactions is determined by the surface, bulk morphology and also the conductivity of active materials. These could be controlled during the preparation of materials. Among various kinds of conducting polymers, polypyrrole (PPy) can be polymerized electrochemically as a tough film with relatively high electrical conductivity. In the electrochemical deposition, however, the morphology of the films can not be controlled easily. In this report, methods for preparation of porous PPy films by means of electrochemical deposition are mentioned. The films are also characterized in terms of electrochemomechanical deformation such as contraction ratios (strain) and contraction forces (stress).

Photographs in Fig.1 (a) and (b) show images of a scanning electron micrograph (SEM) for electrode and electrolyte sides, respectively, of polypyrrole film prepared by electrochemical deposition[1]. The film was polymerized using an aqueous electrolyte solution of pyrrole, *p*-phenol sulfonic acid (PPS) as the main supporting electrolyte. Ethyl acetate solution consisting of anionic surfactant of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was used as the source of micelle emulsion. The micelle emulsion was added to the main electrolyte solution by the volume ratio of 1:1. The PPyAOT film was electrochemically deposited on Pt electrode by application of constant current 1mA/cm². As can be seen in Fig.1, the surface of PPy film at Pt electrode side is porous with the diameter of approximately 1 μ m. The surface without micelle emulsion is flat and smooth reflecting the electrode surface. Therefore, the porous film is due to the effect of micelle emulsion. The PPy films obtained by this method were rather brittle.

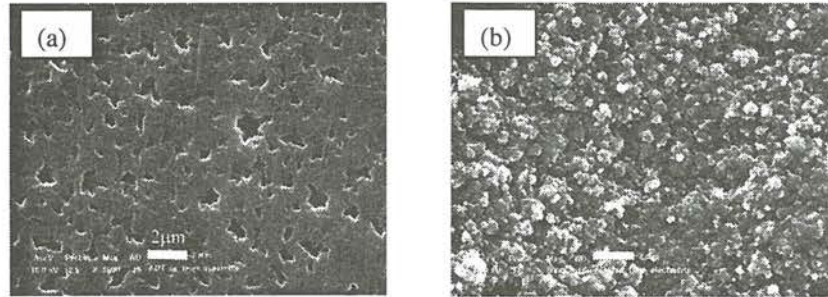


Fig.1 SEM photographs of surfaces of PPyAOT film, (a) electrode side and (b) solution side.

Photographs in Fig.2 are SEM images of PPy films prepared using the organic electrolyte solution of pyrrole and tetrabutyl ammonium (TBA) bis(trifluoromethanesulfonyl)imide (TFSI) in methyl benzoate[2]. The polymerization was carried out at a constant current of 0.2 mA/cm^2 on a Pt anode plate. Thus obtained PPyTFSI films swelled in acetone by 44% in area and shrank by 31% upon dry. The film surface at the electrode side shows beautiful porosity as shown in Fig.2 (a). Contrary to this, the film electrochemically deposited using TBABF₄ or TBACF₃SO₃ exhibited compact and smooth surface[3].

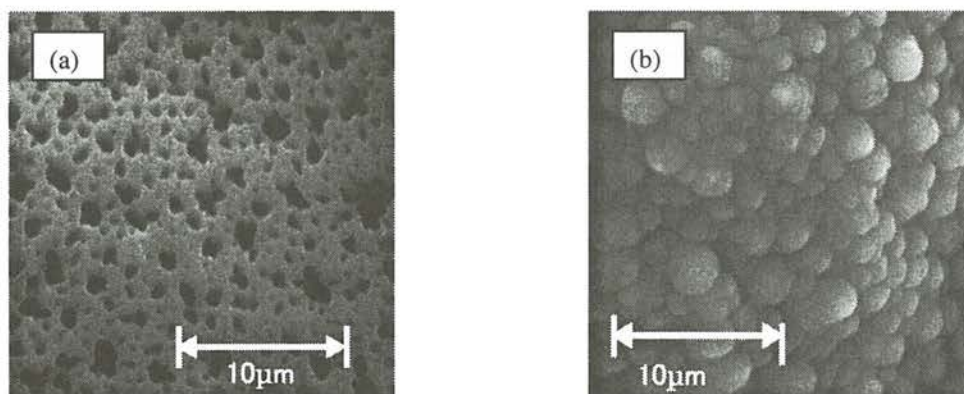


Fig.2 SEM photographs of surfaces of PPyTFSI film, (a) electrode side and (b) solution side.

Figure 3 shows the cyclic voltammogram (CV) and deformation of PPyAOT films operated in electrolyte with various tetra alkyl ammonium chlorides, such as ammonia, tetra methyl (TMA), tetra ethyl (TEA) and TBA. The result showed that the film expands by electrochemical reduction of film (cathodic expansion), indicating doping and dedoping of cation for the reaction. It is noted that large porosity of PPy film enable to be doped with large cation like TMA but not so large for TBA. This fact also indicates that the AOT is immobilized in PPy network and does not contribute as mobile ions upon oxidation. The large cathodic expansion of 4.5% was obtained in 0.2 M TEACl solution, which is compared with our previous results of 1-2 % deformation using metal cations[4].

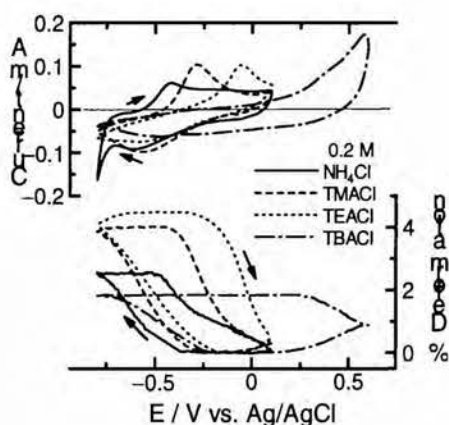


Fig.3 Cyclic voltammogram and %deformation (strain) of PPyAOT films operated in various tetra alkyl ammonium salts at 1 mV/s.

Figure 4 shows the cyclic voltammogram and deformation of PPy TFSI films operated in aqueous electrolyte of LiTFSI solution at scan rate of 2 mV/s. The result showed that the film contracted by 9.1 % for reduction and expanded by 20 % during oxidation of film, followed by contraction by approximately 20 %. The large strain of 20 % should be noted and compared with those of film prepared similarly with TBABF₄ operated in NaPF₆ solution[5] as well as the strain of the natural muscle of 25-30 %. In the PPyTFSI film the electrochemical stress of 6.7 MPa was obtained and is significantly larger than natural muscle of 0.5 MPa and slightly smaller than those of PPyBF₄ film with 22 MPa[5]. The results will be discussed in detail.

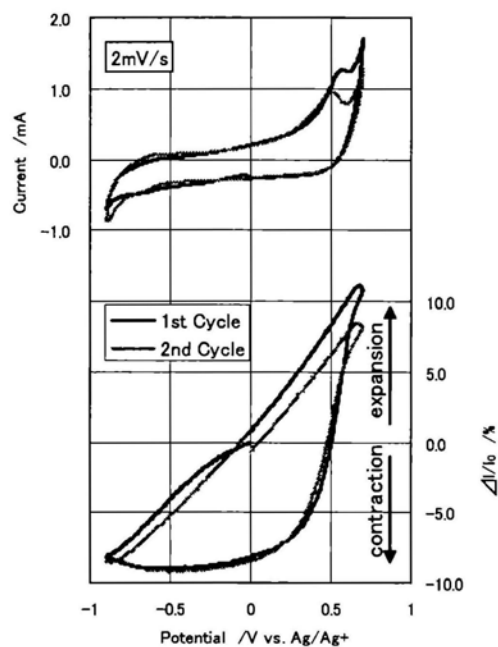


Fig.4.Cyclic voltammogram and strain (%) of PPyTFSI films operated in aqueous LiTFSI solution at 2mV/s.

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