

MORPHOLOGY CONTROL IN ELECTRO DEPOSITION OF POLYPYRROLE FILMS FOR ENHANCEMENT OF ELECTROCHEMOMECHANICAL DEFORMATION, SOFT ACTUATORS

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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. We know that the performances of devices strongly depend on not only the chemical structure of materials and the arrangement of molecules but also the surface morphology.

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 ratio (strain) and contraction force (stress).

Photographs in Fig.1 show surface images of a scanning electron micrograph (SEM) for PPy 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), namely, 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 a constant current 1mA/cm². As shown in Fig.1 (a), the surface of PPy film at Pt electrode side is porous with the diameter of approximately 1µm. The surface without micelle emulsion is flat and smooth reflecting the electrode surface. The PPy films were rather brittle.

Photographs in Fig.2 are SEM images of PPy films prepared using the organic electrolyte solution of pyrrole and tetrabutyl ammonium (TBA) bis(trifluoromethanesulfonyl)imid (TFSI) in methyl benzoate[2]. The polymerization was carried out at a constant current of 0.2 mA/cm² on a Pt electrode. 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 surfaces[3].

Fig.3 shows the cyclic voltammogram (CV) and strain of PPyAOT films operated in electrolytes of ammonia, tetra methyl (TMA), tetra ethyl (TEA) and TBA. Results showed that the film expands by electrochemical reduction (cathodic expansion). It is noted that large porosity of PPy film enables to be doped with large cations like TMA but not for TBA. This fact also indicates that the AOT is immobilized in PPy network. 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.4 shows the CV and deformation of PPy TFSI films operated in aqueous electrolyte of LiTFSI solution at scan rate of 2 mV/s. The results showed that the film expanded by more than 20 %, which is 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].

References

- [1]W. Takashima et.al. Chem. Letts., in press (2004).
- [2]S. Hara et. al., J. Material Chem. **14**, 1516 (2004).
- [3]S. Hara et. al., Polym. J. **36**, 151 (2004).
- [4] W. Takashima et. al. Jpn. J. A. P. , **41**, 7532 (2002).
- [5]S. Hara et. al., Chem. Letts., **32**, 576 (2003).

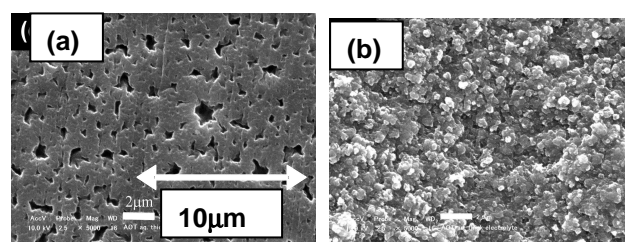


Fig.1 SEM photographs of surfaces of PPyAOT film, (a) electrode side and (b) solution side. Both are same Mag.

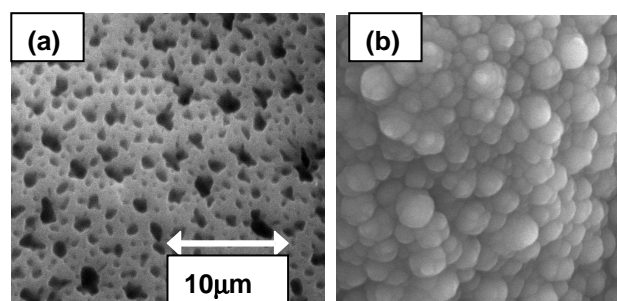


Fig.2 SEM photographs of surfaces of PPyTFSI film, (a) electrode side and (b) solution side. Same Magni

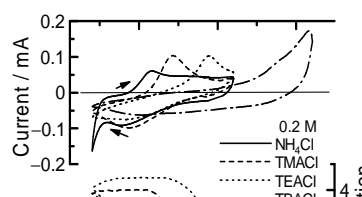


Fig.3 CV and %strain of PPyAOT films operated in various tetra alkyl ammonium salts at 1 mV/s

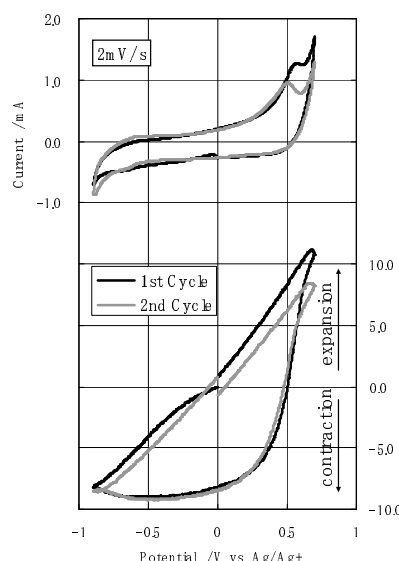


Fig.4 CV and %strain of PPyTFSI films operated in aqueous LiTFSI solution at 2mV/s.