

Enhanced Swelling Behaviors of Polypyrrole Film Doped with Sulfonated Polyaniline

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Polypyrrole (PPyDBS/PMAS) films partially doped with poly(2-methoxyaniline-5-sulfonate) (PMAS) have been deposited in dodecylbenzene sulfonic acid solutions. Both of the conductivity and water content of the film were found to show the strong dependence of PMAS contents, indicating that the PMAS was clearly incorporated and strongly affects the film characteristics. The obvious increase of cathodic expansion (4.5% in expansive strain) for PPyDBS/PMAS (5%) film elucidates that the PMAS additive contributes to improve the cathodic expansion, which can be attributed to the increased swelling capability of PPy with PMAS incorporation.

Soft actuator fabrication using conducting polymer has attracted much attention for developing artificial muscles.¹ Some attractive new improvements²⁻⁴ have been developed by many researchers. A new type of bending mechanism also has been proposed, by which a large bending was realized.⁵ In such device both of the anodic and cathodic expansions are required to possess the similar deforming performance for the stable actuation.⁶ The cathodic expansions, however, are commonly smaller than the anodic expansion.⁷ It probably associates that the anion exchange is a simple ejection of dopant, while the cation exchange is a charge compensation in the reduction state for remaining counter anion.^{5,8,9} Such difference suggests the high compactness of cation exchange film. Concerning the ion size effect embedded in the film,^{10,11} the large cation seems to be difficult to exchange the compact film.

Various polymers substituted with sulfonate have been used as counter anion. However the insulating feature of dopant strongly decreases the film conductivity. Sulfonated polyaniline (SPAN) is expected to dope as well as to maintain the film conductivity. Doping effect on PPy with conducting polymer is also interesting. PPy doped with dodecylbenzene sulfonate (PPyDBS) is known to show the cathodic expansion because of the strong entrapment of DBS.^{5,7} The comparison between the cathodic expansions doped with SPAN and DBS will clarify the effect of SPAN incorporation. This study reports the PPy film deposited from aqueous media containing DBS as well as poly(2-methoxyaniline-5-sulfonate) (PMAS).¹² PMAS being polymerized with its monomer, the PMAS contents in the electrolyte can be controlled precisely. In this study, we report the effects of partially incorporated PMAS on electrochemomechanical deforming (ECMD) characteristics of PPy.

PMAS incorporated PPy films were deposited galvanostatically in aqueous electrolyte containing DBS mixing with various amounts of PMAS, in which the total number of sulfonate substitution is fixed at 0.1 M. In this study molar ratio of sulfonate substitution of PMAS represents the PMAS content. 0.1 M of distilled pyrrole monomer was dissolved in the electrolyte. Ex-

cept pyrrole, all the other chemicals were used without further purification. An AgCl-coated Ag wire and a Pt foil-rolled Pt wire were used as reference and counter electrodes, respectively. PPyDBS/PMAS films deposited on stainless steel were stored in water before use. Direct measurement system of film deformation⁷ was employed for the ECMD behavior with cyclic voltammetry (CV). Potential was swept with 5 mV/s for all the CV measurements. Film conductivity was measured with four electrode method after drying. Water contents of the film were estimated with the change of film weight before and after drying in vacuo.

The film conductivity was decreased from 46 to 2.7 S/cm with increasing the PMAS content from 0 to 50%, which was stationary over 50% (Table 1). It should be noted that the PPy could be deposited with high current densities (4–8 mA/cm²) in the electrolyte having over 50% PMAS, which might cause the decrease of film conductivity as well as mechanical strength.^{13,14} It is noteworthy that the film conductivity was almost stationary before and after drying, indicating that the PPy moiety mainly determines the conductivity of PPyDBS/PMAS film. Water content was increased from 60 to 97% with increasing the PMAS contents. PMAS being the water soluble, the PMAS incorporation should increase the water capacity.

The mechanical properties strongly decreased in the film having large amount of PMAS contents. In the case of the film deposited from the electrolyte containing 5% PMAS (PPyDBS/PMAS (5%)), the film retains the relative high conductivity as well as large mechanical strength. Therefore, PPyDBS/PMAS (5%) was used as the target sample to compare the deformation magnitude with and without of PMAS content. Figure 1 shows the CV and simultaneously obtained ECMD curves in the PPy films. The result elucidates that the PMAS incorporation clearly changed the ECMD characteristics. The PPyDBS film exhibits to show the simple cathodic expansion of 1.0%, which is the similar magnitude as reported in the literature.⁷ In the PPyDBS/PMAS (5%) film, however, the ECMD characteristics have complicated.

Table 1. Electronic conductivity and water content of the PPy film electrodeposited from the mixture of DBS having various contents of PMAS

PMAS /mol %	Current Density /mA/cm ²	Conductivity /S/cm	Water Content /wt %
0	1	46	60
5	1	15	71
10	1	8.0	90
50	4	2.7	93
100	8	2.0	97

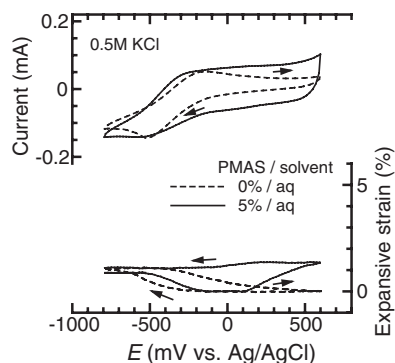


Figure 1. CV and ECMD curves of PPyDBS films deposited with and without PMAS content in aqueous solution containing 0.5 M KCl.

A subtle perusal corroborates that the film exhibited an anodic contraction from -500 to 200 mV followed with an anodic expansion from 100 to 600 mV during the oxidation process, while a quite small contraction was only observed during the reduction process. In CV curves, the larger redox current was observed in the PPyDBD/PMAS (5%) film as compared to that in the PPyDBS film. The results indicate that the incorporated PMAS fairly affects on both the deformation and redox characteristics.

It should be noted that the PPy film having co-expansive behaviors at both the anodic and cathodic potentials consistently exhibits a set of contraction followed by expansion during both of the oxidation and reduction processes.⁹ This can be explained by a sequential occurrence of anion ejection followed by cation injection at different potentials, which suggests that the cation injection and anion ejection in PPy film correlate with each other by some osmotic contributions,¹⁵ inhibiting the individual exchanges of both ions. In PPyDBS/PMAS, however, the deforming behaviors during the reduction process were ruled out. The PMAS is incorporated as polyanion, in which some sulfonate substitutions substantially play as the counter anion. The polyaniline (PAni) moiety in PMAS is, therefore, free from the PPy doping, which will survive the redox reaction of PAni. The novel deformation in PPyDBS/PMAS, therefore, should be attributed to the convoluted redox reactions at both the PPy and PAni moieties.

Figure 2 shows the CV and ECMD curves in non-aqueous media. In 0.5 M tetrabutyl ammonium BF₄/ethyl acetate (TBABF₄/EA) solution, the PPy films exhibited the cathodic expansion even in the film involving PMAS, in which the deformation magnitude rather increased. PAni has been reported to show the anodic expansion in the acidic media,¹⁶ which was however commonly decreased in its electrochemical activity as well as ECMD activity in non-aqueous media.¹⁷ The drastic change of ECMD characteristics as well as CV curves from Figures 1 and 2, therefore, can be attributed to the suppression of redox activity of PMAS in the film with the solvent exchange. It is interesting to note that the cathodic expansion of PPyDBS/PMAS (5%) film is rather increased to be around 2.9% in ethyl acetate (EA) as compared to that of the same film in aqueous media (1.6%). It was reported that tetra-alkyl ammonium decreases to inject the PPy film with increasing the alkyl length.¹¹ In particular, TBA⁺ is difficult to inject PPy because of its high bulkiness.^{5,18} The reversal injection of TBA⁺ as well as cathodic ex-

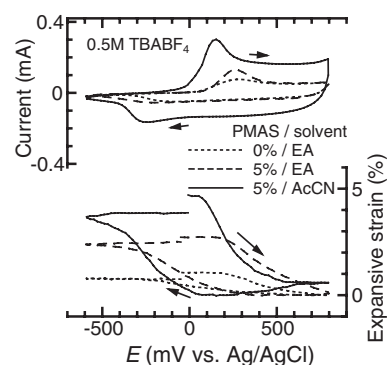


Figure 2. CV and ECMD curves of PPyDBS films with and without of PMAS content in non-aqueous solutions containing 0.5 M TBABF₄.

pansion has been reported for only Aerosol OT incorporated PPy film (PPyAOT),¹¹ although the amount of injecting TBA⁺ is small. An anodic peak was also appeared at high voltage of 590 mV in PPyAOT as compared to those (from 120 to 250 mV) of PPyDBS/PMAS (5%) in Figure 2. The results indicate that PMAS additive fairly affects to enhance the capability for injecting the large cation, TBA⁺, in PPy. Optimization for the preparation of electrolyte is under investigation for further improvement of cathodic expansive behavior.

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