Improved Cathodic Expansions of Electrochemomechanical Behavior in Polypyrrole Films Electrodeposited from Aerosol OT Emulsion

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(Received April 7, 2004; CL-040380)

Electrodeposited polypyrrole films in Aerosol OT emulsion media (PPyAOT) have been investigated in terms of their electrochemomechanical characteristics for various tetraalkyl ammonium (TAA) chloride salts. PPyAOT film exhibited a cathodic expansive behavior during potential cycling, indicating the reversible exchange of TAA in PPyAOT. The oxidation peaks changed with the alkyl chain length while the reduction peaks were stationary. The large cathodic expansion of 4.5% was obtained in 0.2 M tetraethyl ammonium chloride solution. The unique porous morphology on PPyAOT film seems to assist the large mobility of bulky cations.

The development of soft actuators fabricated by conducting polymers has attracted much attention because of their practical application for artificial muscles. Amongst conducting polymers (CPs), polypyrrole (PPy) is one of the most investigated materials because of its ease in the film preparations and retention of electrochemomechanical activity at the neutral pH. Both the anodic and cathodic expansions in PPy are also observable by judicious selection of the supporting electrolytes for the film deposition. In general, deformation magnitude for cathodic expansion tends to be small as compared to that of anodic one. The small deformation magnitude in CP actuators offers a large stumbling block towards their practical usage. Therefore, a variety of investigations and efforts towards the enhancement of magnitude of deformation have been carried out by many researchers.[1–3]

There are several reports pertaining to the chemical synthesis of CPs in the micellar media.[4] The anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) is an interesting material because of the reverse micelle formation.[5] There are several reports to use AOT in the chemical synthesis of PPy,[6,7] while the electrodeposition of PPy in the AOT micellar electrolytes has not yet been reported. In particular, the electrochemomechanical deformations (ECMD) in the film deposited from the emulsion are attractive for actuator fabrication owing to the possibility for the film having large porosity. The electrodeposition in the micellar electrolyte is regarded as one of the approaches to fabricate the film with the large deformation, because the films thus obtained possesses the porous or unique structures.[7]

Here, we report the ECMD characteristics of PPy electrodeposited in the mixture of aqueous and nonaqueous solutions with AOT. The deformation magnitudes are compared in terms of the cation size of tetraalkyl ammonium chloride (TAACl) salts.

Aqueous solution was prepared by dissolving 0.25 M of *p*-phenol sulfonic acid (PPS) with 0.15 M of distilled pyrrole monomer. Nonaqueous solution was prepared by dissolving 0.5 M of AOT in ethyl acetate. Both electrolytes were mixed in the volume ratio of 1:1, in which the electrodeposition was carried out for fabricating the freestanding PPy film (PPyAOT). Cyclicvoltammetry (CV) was performed in the custom made electrochemical cell for observing the ECMD behavior with the in situ measurement system described earlier.[1,8] ECMD characteristics were evaluated in various aqueous solutions having 0.2 M TAACl. The effect of alkyl chain length of TAA$^+$ on the ECMD performance was evaluated.

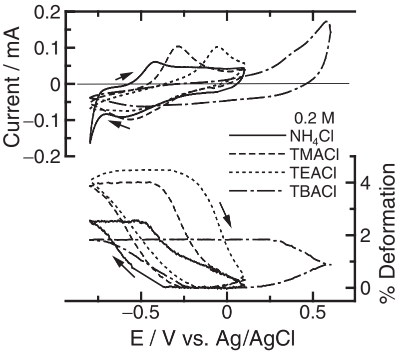

Figure 1. Cyclic voltammograms and electrochemomechanical deformation curves of AOT doped PPy films in variety of tetraalkyl ammonium chloride salt solutions (0.2 M).

PPyAOT exhibited the cathodic expansion (3%) in 1 M NaCl solution. Even after potential cycling, the stable cathodic expansion was observed. This should be compared with the PPy deposited in *p*-phenol sulfonic acid (PPyPPS), in which the transition from cathodic to anodic expansion was occurred with potential cycling.[9] In the electrolyte solutions having large anion such as ethylbenzene sulfonic acid sodium salt (NaEBS), the PPyAOT films clearly exhibited the cathodic expansions and well-defined CV curves, indicating that the relatively large anion such as EBS$^-$ never depresses the redox activity in PPyAOT.[9] This elucidates that the cations are the dominant mobile ions in the PPyAOT. The typical cathodic expansive film, dodecylbenzene sulfonate doped PPy (PPyDBS), tends to show a small deformation magnitude of around 1.0–2.0%.[8] The cathodic expansion of 3% in PPyAOT, therefore, regards to be larger than that in PPyDBS and a little small as compared to that reported by Skaarup et al.[3]

Even in the tetrabutyl ammonium chloride (TBACl) solution, PPyAOT exhibits the cathodic expansion at ambient temperature (Figure 1). It has been reported that in PPyDBS, the redox currents as well as the film deformations were not observed in the electrolyte having the bulky cation such as TBA$^+$.[10,11] The comparison of the cathodic expansive behaviors in both PPyAOT and PPyDBS films corroborates this PPy film has the different threshold size for the mobile ions,[12] which will be defined by the fabrication procedure. The electrodeposited PPy films in the micellar emulsion with AOT, therefore, improve the capability of the film towards the insertion and deinsertion of large cations as compared to that of PPyPPS, which directly enhances the cathodic expansion.

Table 1. Redox peak potentials and deformation magnitudes for PPyAOT film in various electrolyte solutions (0.2 M)

	V_{oxd}/V	V_{red}/V	ΔV/V	Q/mC/mm^3	*Def.*/%
NH_4Cl	−0.42	−0.60	0.18	138	2.6
TMACl	−0.29	−0.57	0.28	119	4.0
TEACl	−0.05	−0.60	0.55	102	4.5
TBACl	0.59	−0.49	1.08	159*	1.8

*Collected at the different potential window.

As listed in Table 1, the potential difference from oxidation to reduction (ΔV) increases as a function of alkyl chain length, indicating the decrease in speed of redox reactions. This also clarifies the mobile ions are the TAA^+ cations in this system. The similar maximum of deformation magnitude was found in both 0.2 M tetramethyl ammonium chloride (TMACl) as 4.0% and 0.2 M tetraethyl ammonium chloride (TEACl) as 4.5%, while in 0.2 M TBACl the lower magnitude of 1.8% was obtained. It should be noted that the oxidation peaks were shifted towards the higher potential while the reduction peaks were almost stationary, suggesting that the "ejecting" speed of cation is dominantly depressed as a function of cation size.

For investigating the electrolyte effect on ECMD behavior, CV measurements should be performed in the same potential window. In TBACl, however, the monotonic film expansion was only observed when potential was scanned from −650 to 100 mV vs Ag/AgCl. For the comparison of deformation magnitude, therefore, the wide potential window was employed for 0.2 M TBACl. It should be noted that the contractive creep during CV cycling was obtained in NH_4Cl, TMACl, and TEACl solutions, while the expansive creep was observed in TBACl solution. This indicates that some penetrated TBA^+ will be trapped and accumulated in PPyAOT net during potential cycling. The strong decrease of "ejecting" speed also supports such TBA^+ trapping model. This phenomenon induces the decrease of cathodic expansion and potentially alternative increase of anodic expansion. Coexpansive behaviors at both the anodic and cathodic potentials predict the strong depression of film deformation, which well explains the small cathodic expansion despite the large redox charge in TBACl. Therefore, the retention of monoexpansive characteristics should be required for achieving the enhancement of ECMD. Consequently, for the increase of deformation, large mobile ion is required; however, in the electrolytes having the extra large ion such as TBA^+, the film deformation tends to decrease because of some entrapment effect.

Similar discussion will be taken into the comparison of ECMD magnitudes in TMACl and TEACl solutions. The ECMD magnitude should change with both the size of exchanged ion and the potential window. Therefore, the listed results are the values obtained under the condition employed in this study. The accurate judicious selection of the measurement condition is required for the precise comparison of ECMD.

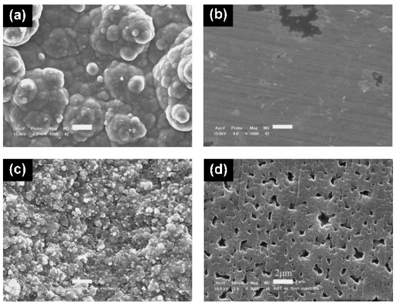

Figure 2. Scanning electron micrographs of electrodeposited film surfaces: (a) solution side of PPyPPS, (b) electrolyte side of PPyPPS, (c) solution side of PPyAOT and (d) electrolyte side of PPyAOT, respectively. Inserted white bar represents 2 μm in scale.

The SEM micrographs revealed that the PPyAOT films have the unique surface morphologies. The comparison of film surfaces to the electrolyte side corroborates that the PPyAOT films has the fine porous structure as compared to that of PPyPPS. In the case on the substrate side, the PPy films have been reported to have the flat surfaces. Considering the strong adherence to the substrate during deposition, the film surface should be replicated from substrate structure (Figure 2b). While, the PPyAOT film was found to show large and small voids having their diameter up to 1 and 0.1 μm, respectively (Figure 2d). The generation of the fine porous structure on both surfaces is pertaining to the AOT emulsion as reported in the literature.[6] Such unique morphologies will explain the enhanced capability in size of mobile cations such as TMA^+ and TEA^+, which contributes to enhance the deformation magnitude in PPy film. The detail analysis in terms of the morphology and porosity in PPyAOT is still required for further investigation.

Authors express their thanks to Eamex Co. for financial support.

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