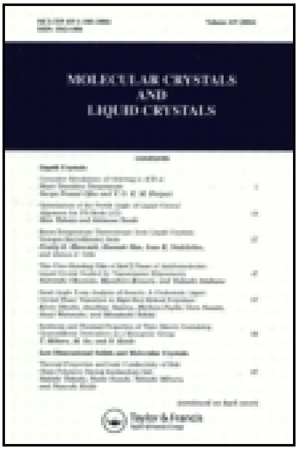

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Redox Behavior of Polypyrrole Films in Different Solvents

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REDOX BEHAVIOR OF POLYPYRROLE FILMS IN DIFFERENT SOLVENTS

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Abstract The redox behavior of polypyrrole (PPy) films has been examined by means of cyclic voltammetry and SEM/EDS. PPy was galvanostatically prepared in acetonitrile (AN) containing tetrabutylammonium dodecylsulfate (TBADS) as an electrolyte. Charge compensation mechanism of PPy films which incorporate dodecylsulfate (DS) ions was greatly influenced by the solvents or electrolyte used in the redox reaction. When the PPy was switched between -0.8 V and 0.5 V in the TBADS/AN solution, bulky DS ions were participated in the redox reaction of the swollen PPy film. In the aqueous solution containing NaDS, on the other hand, Na cations worked as main charge-compensating ions because DS anions with long alkyl chains were trapped in the contracted PPy and difficult to move during the switching process. However, DS ions in the TBADS/water solution should be the compensating ions to show higher oxidation potentials. When the free-standing films were reduced for 24 hours at -0.8 V against an Ag/AgCl reference electrode in the TBADS/AN solution, EDS sulfur concentration profiles showed that DS anions were removed from the films, which lead to a reduction in film thickness to two thirds of the original thickness but in the aqueous solutions there was no change in film thickness upon reduction. The initial redox reaction in the TBADS/AN solution was most reversible and reactive but long term cyclability (electrochemical stability) of the PPy films in AN was inferior to that in water, which resulted from the morphological collapse during the repeated redox reaction.

INTRODUCTION

Since Diaz et al.[1] electrochemically prepared strong polypyrrole (PPy) films on a platinum electrode in 1979, PPy has raised great interests due to the convenience of its formation by electrochemical polymerization and high stability against air and heat.[2-4] It has been considered as a promising material in applications to rechargeable battery, [5, 6] electrochromic display[7] and molecular electronics.[8] Among the important properties in these applications is the electroactivity of redox reactions, which is the property to switch reversibly between a conductive state and an insulating state by cycling voltage. The electroactivity during the switching process results from electron transfer and diffusion of doping or charge-compensating ions in the bulk of PPy films.[9] Kinetics of the redox reaction is primarily controlled by the slow diffusion rate of ions through the bulk of PPy films during electrochemical reaction.[3, 10] Much work has been done on the charge-compensation mechanism for the PPy films where small anions are believed to transport through the PPy bulk for achieving electroneutrality in the film.[11] However, recent reports have shown cases that cations instead move into the bulk of PPy films to maintain the electroneutrality on reduction.[12-14] For example, when polymeric[12, 13] or bulky anions[14] are incorporated in the production of PPy films, relatively small cations in the solution diffuse into the film on reduction of the polymer as charge-compensating ions.

In this study we report the details of redox reaction of PPy films doped with an anion of a long aliphatic chain in different solvents. To elucidate the charge-compensating mechanism elemental concentration of dopants and change in PPy film morphology upon reduction were further characterized. PPy films were prepared in acetonitrile (AN) but electrolysis was done both in an organic solvent and in aqueous solutions. The cyclic voltammetric technique was used to determine the electrochemical behavior of PPy films such as electroactivity and electrostability. Morphology change upon reduction was investigated by scanning electron microscope (SEM). Energy dispersive X-ray spectrometer (EDS) was employed to determine the elemental concentration profiles of dopants or charge-compensating ions in the PPy film.

EXPERIMENTAL

Pyrrole monomer and AN were dried and purified as described elsewhere[15] and tetrabutylammonium dodecylsulfate (TBADS), used as an electrolyte, was synthesized in our laboratory.[16] PPy was formed galvanostatically on a platinum electrode (3 X 6 cm^2) in a one-compartment cell containing 0.036 M TBADS and 0.36 M pyrrole in AN. The current density was maintained at 2.0 mA/cm^2 for 2 hours to obtain about an 80 μm–thick free-standing film. The film on the platinum electrode was peeled off and thoroughly rinsed in AN for a couple of hours. For studies of morphology and elemental concentration profiles of dopants as well as charge-compensating ions the peeled free-standing film was electrochemically discharged in AN containing 0.036 M TBADS or in an aqueous solution containing

0.036 M TBADS or sodium dodecylsulfate (NaDS). The applied potential was -0.8 V with respect to an Ag/AgCl, KCl (saturated) electrode for 24 hours.

For studies on electrochemical behavior, thin PPy films were prepared on a platinum electrode (1 X 1 cm^2) at the same conditions as the thick film preparation except current density. Current density was kept constant at 5 mA/cm^2 and polymerization times were varied to obtain films of various thicknesses equivalent to 0.05, 0.10, 0.30, 0.50 and 1.00 C/cm^2. The PPy film on the electrode was rinsed in AN and dried in a vacuum oven. Cyclic voltammograms were obtained using a potentiostat (Hokuto Denko model HA-301) along with a function generator (Hokuto Denko model HB-104) and an XY recorder (Linseis model LY 1800). The electrolyte concentration in the electrochemical study was 0.1 M to reduce solution resistance.

Morphology and elemental concentration of dopants along the cross section of PPy films were obtained by using SEM (Hitachi 2500C)/EDS (Kevex delta V). All the PPy films were carbon-coated to avoid the charging problem.

Results and Discussion

Figure 1 shows cyclic voltammograms (CVs) of PPy films on a platinum electrode during polymerization in the TBADS/AN solution (a) and in the NaDS/water solution (b). Potential sweep was done at a scan rate of 50 mV/sec from -0.50 V to 0.85 V in the TBADS/AN solution and from -0.70 V to 0.60 V in the NaDS/water solution, respectively. The monomer oxidation, represented by big sharp peaks at the right end, takes place at a less positive potential in water due to better stability of electrogenerated radical cations by more nucleophilic water molecules.[17] The oxidation potential of polypyrrole (E_{pa}) is lower than that of monomer (E_{ma}), which makes simultaneous doping possible during electrochemical polymerization. The PPy film prepared in AN shows better electrochemical reversibility, which is indicated by a smaller peak potential difference ($\Delta E_p = E_{pa} - E_{pc}$) and a sharp oxidation peak of the polymer. These observations are summarized in Table I.

Table I Electrochemical Parameters of PPy Films During Polymerization.

polymerization solution	E_{ma}, mV	E_{pa}, mV	E_{pc}, mV	ΔE_p, mV
TBADS/AN	700	-210	-270	60
NaDS/water	500	-460	-580	120

The effect of switching potential on electrochemical activity of the PPy film is shown in Figure 2 and the activity may be represented by the redox peak height. The PPy films were galvanostatically prepared on a Pt electrode with a charge of 0.05 C/cm^2 in the NaDS/water solution. When the switching potential from oxidation to reduction is 0.5 V in the NaDS/water solution, the electrochemical activity shows almost no change during scans (up to 15) as shown in Figure 2a. However, when the switching potential is extended to 1.0 V, another big oxidation peak appears at around 0.8 V but the following peaks become smaller on subsequent scans (Figure 2b). The smaller redox peak currents with increasing scan numbers suggest that a large part of the film was over-oxidized to lose its activity. Thus the oxidation peak at around 0.8 V resulted from electrochemical reaction of the PPy film, which experienced destruction of the PPy structure and released soluble materials. : when the PPy was kept at 1.0 V, the solution around

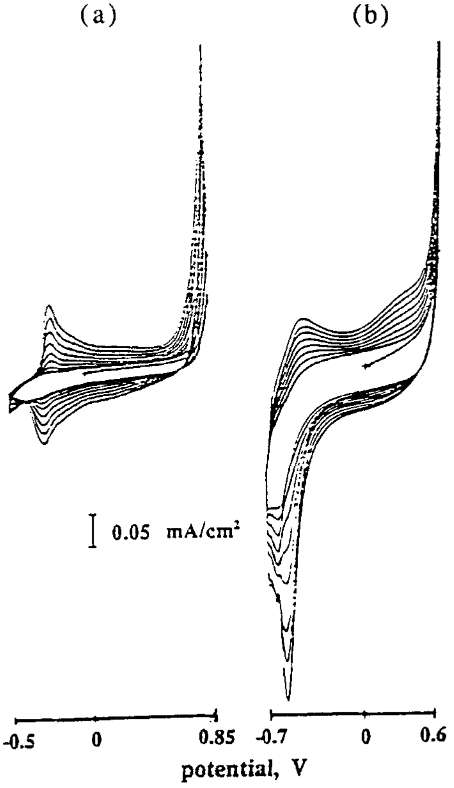

Figure 1 Growth CVs for PPy film in (a) AN containing 0.1 M TBADS and 0.36 M pyrrole and (b) aqueous solution containing 0.1 M and 0.36 M pyrrole.

the PPy film became purple in a few seconds. The result suggests that a proper potential window exist in the PPy films when used as an electrode material.[18]

CVs with increasing scan rates for the PPy films in different electrolyte/solvent systems are shown in Figure 3 and electrochemical parameters obtained in each solution are listed in Table II. All the PPy films are prepared in the TBADS/AN solution by applying the fixed charge of 0.05 C/cm^2. Each PPy film was first reduced at -0.8 V in the given solution system against an Ag/AgCl reference electrode for 10 sec and then scanned between 0.5 V and -0.8 V at various scan rates : scan rates were 20, 30, 50, 70 and 90 mV/sec in series. All the CVs exhibit several characteristic features : 1) peak currents are proportional to scan rates, which will be discussed in detail in the following section, 2) the film in the TBADS/AN solution shows sharp, well defined redox peaks as shown in Figure 3a, indicating electrochemically more reversible characteristics than those in water, 3) the PPy film in the TBADS/water solution shows smaller and broader peak currents, especially during reverse scans as shown in Figure 3b. The much smaller and broader cathodic currents compared to the anodic currents indicate that some of the electroactive sites may be irreversibly lost during a reductive scan by forming electrochemically inactive products. Also the film in the TBADS/water solution has the highest oxidation potential compared to the others. In this case the ions involved in the oxidation reaction must be TBA cations, DS anions or both in the electrolytic solution. The high oxidation potential may mean that diffusion of counter ions through the film is slow or difficult in the TBADS/water solution, and 4) the film in the NaDS/water solution reveals two redox peaks as shown in Figure 3c. The peak potential at the right side on the oxidative scan, which is close to that observed in the TBADS/water solution, seems to be related to bulky DS anions since there is no TBA cation in the system. The sharper redox peaks at the lower potential which are not shown in Figure 3b must be associated with Na

Table II Electrochemical Parameters at The Scan Rate of 50 mV/sec for PPy Films Prepared in AN.

polymerization solution	electrolysis solution	E_{pa}, mV	E_{pc}, mV	ΔE_p, mV
TBADS/AN	TBADS/AN	-220	-330	110
	TBADS/water	-50	-300	250
	NaDS/water	-420	-500	80
		+135	-180	315

reduced in TBADS/AN solution.

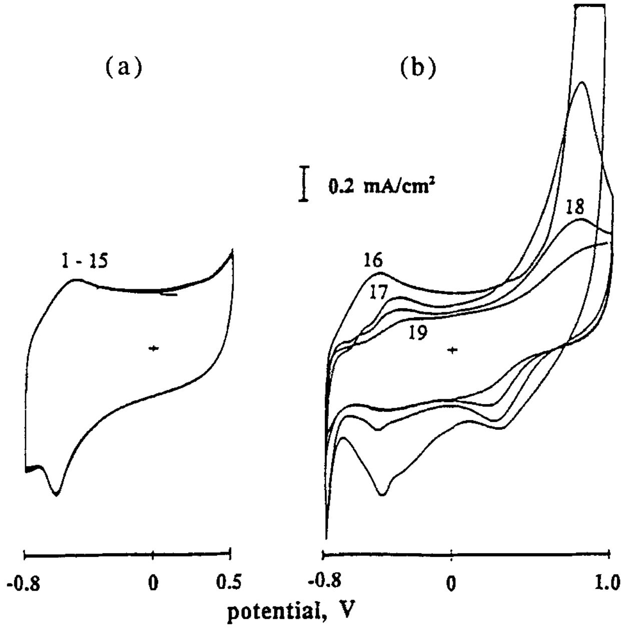

Figure 2 Effect of switching potential on electroactivity of PPy film in NaDS/water system: (a) switching potential = 0.5 V and (b) switching potetial = 1.0 V.

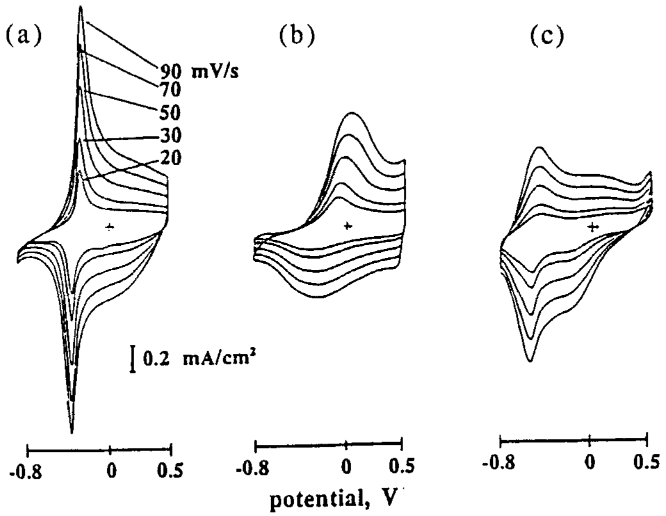

Figure 3 Scan rate dependence of CVs for PPy films in different solutions: (a) TBADS/AN system, (b) TBADS/water system and (c) NaDS/water system.

cation. Since DS ion imbedded in the PPy hardly leaves the polymer upon reduction in the aqueous solution, Na cation moves into the PPy bulk to neutralize the freed DS ion.[18] Thus, in the aqueous solution there seems that most redox sites are balanced by Na cations and only the surface sites are controlled by the DS anions.

To study further electrochemical kinetics based on the above observations, anodic peak currents, obtained from cyclic voltammograms for five different film thicknesses, were plotted on a log-log scale as a function of the scan rate for each solution. One of the plots for TBADS/AN solution is shown in Figure 4. The slopes calculated for PPy films in each solution, which depend on the rate controlling step in the whole redox process, are presented as a function of film thickness in Figure 5. It is known that surface-controlled reaction shows the slope of 1.0 while semi-infinite diffusion controlled redox reaction of 0.5.[15] Figure 5 shows that the slopes vary from 1.0 for the very thin films to about 0.6 for the thick films and their variation is quite different from solution to solution. Since the slopes due to Na cation for the films in the NaDS/water solution are close to 1.0 even for relatively thick films, electron transfer process of the PPy film in the NaDS/water solution is similar to that observed in a thin layer cell.[15] It seems that the rate of the electron transfer depends little on the film thickness in the NaDS/water solution. In other words the small charge-compensating species freely move through the film bulk. In the other solutions except for very thin films the electrochemical process has mixed characteristics observed both in a thin layer cell and under a semi-infinite diffusion condition.

To clarify which is involved as a charge-compensating ion in the switching process of the PPy films prepared in AN was EDS employed. Free-standing films were reduced in the different solutions at -0.8 V against the reference electrode for 24 hours. Then, EDS sulfur concentration profiles were taken from the cross sections of the films and are presented in Figure 6. When the PPy film prepared in the TBADS/AN solution was reduced in the same solution, the sulfur content is greatly reduced upon dedoping as shown in Figure 6c, indicating that bulky DS anions imbedded in the film were expelled from the film during the 24 hour reduction. However, the PPy film reduced in the aqueous solution containing NaDS or TBADS, shows a negligible change in the sulfur concentration compared to that of the pristine film. A presence of Na cations in PPy upon reduction in the NaDS/water solution confirms that the freed DS ions should be neutralized by Na cation present in the aqueous solutions since DS ions hardly leave the polymers upon reduction.[18] However, in the TBADS/water solution there seems to be competition between TBA cations and DS anions in balancing the charge in the polymer on the redox reaction. DS anions are probably the main charge-compensating ions based on the peak position of DS anions as shown in Figures 8a and 8c.

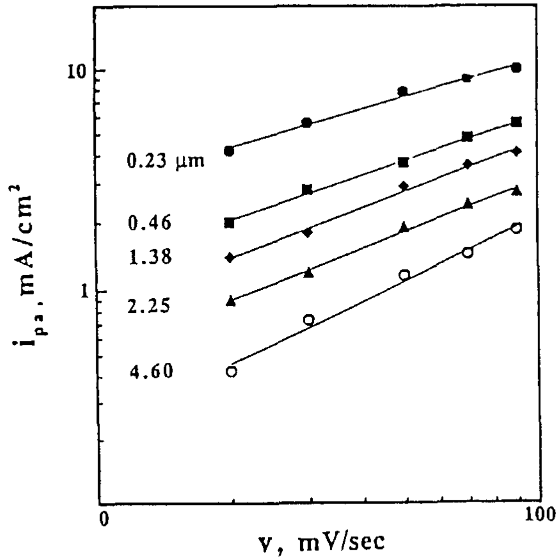

Figure 4 Anodic peak currents as a function of scan rate for PPy films in TBADS/AN solution.

Judging from the size of charge compensating ions, it is very surprising to note that the PPy film in AN solution is electrochemically most reversible as well as most reactive as shown in Figure 3. However, if the role of solvent in ion transport through the PPy bulk films is considered, the above result could be explained : the PPy film in AN is swollen and even the large anions with a long hydrophobic alkyl chain can easily transport in the film. This speculation is also consistent with Schlenoff's marked dependence of redox kinetics on solvent.[10] However, once the bulky dopants were expelled from the PPy film, the PPy films was not morphologically stable enough so that it collapsed with prolonged reduction. This was confirmed by SEM micrographs : when the free-standing film was dedoped for 24 hours in the TBADS/AN solution and dried, the film thickness was reduced to two thirds of the original thickness due to the removal of DS anion as shown in Figure 7 but in the aqueous solutions where the polymers are swollen little, the original thickness was almost preserved. Therefore, when a bulky DS anion is incorporated in the PPy films, the results of EDS and CV demonstrate that the charge compensating mechanism is controlled by the solvent or electrolyte used. In other words, when AN was used as the solvent the polymer is swollen and PPy molecules are packed loosely so that the anions easily come out of films during the reduction process. On the other hand, when the same experiment was

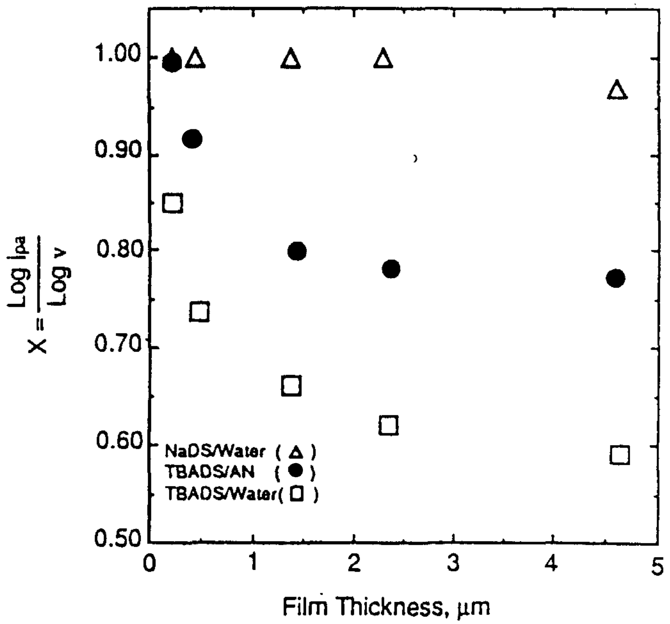

Figure 5 Relationship between slopes and film thickness in different solutions.

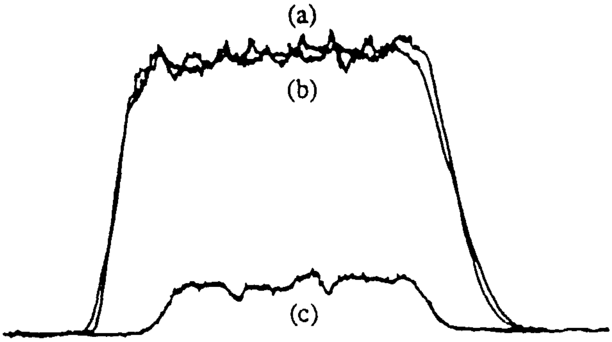

Figure 6 EDS sulfur line profiles taken from the cross section of PPy films: (a) polymerized, (b) reduced in TBADS/water solution and (c) reduced in TBADS/AN solution.

done in the NaDS/water solution, bulky DS anion with a hydrophobic alkyl chain is trapped inside the film and difficult to move out. Therefore, cations probably Na cations must diffuse into the films to neutralize the anions freed from the neutralized polymer. However, DS anions rather than TBA cations in the TBADS/water solution seem to be involved in the redox reaction.

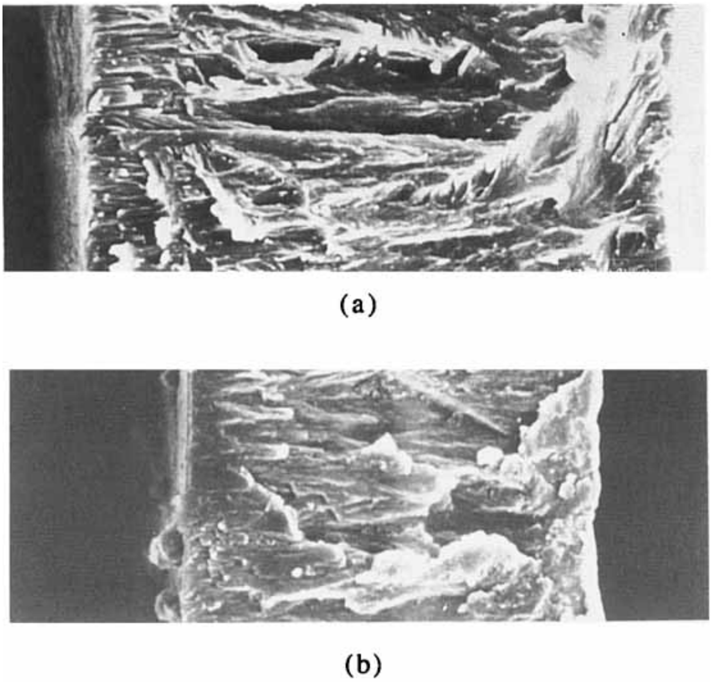

Figure 7 SEM micrographs of PPy films: (a) polymerized and (b) reduced in TBADS/AN solution.

Electrochemical cyclability of PPy is a very important factor for applications. CVs were recorded as a function of scan numbers and are shown in Figure 8. When PPy was cycled in the AN solution, anodic peak currents decrease very rapidly and almost disappear after 300 cycles as shown in Figure 8a. This result may be explained by the fact that once the bulky DS anion diffuses out of the film slowly with increasing scan numbers, the swollen film slowly collapses. The intermolecular interaction force is so large that subsequent oxidation fails to bring the dopant to the vacated sites. This is the reason why the redox reactivity goes down with repeated redox cycles. However, when the films are scanned in the aqueous systems, there still retain peak currents until the 3400th cycle though there are some reductions in peak heights as shown in Figures 8b and 8c. The clue for preservation of the electrochemical reactivity after prolonged redox cycles is not clearly pointed out yet but the film morphology seems important for transportation of DS anions or Na cations through the PPy bulk. In the latter cases PPy films change color from transparent green on reduction to brownish black on oxidation even at the 3400th cycle but the former film did not show any electrochromism and became black at the 300th cycle.

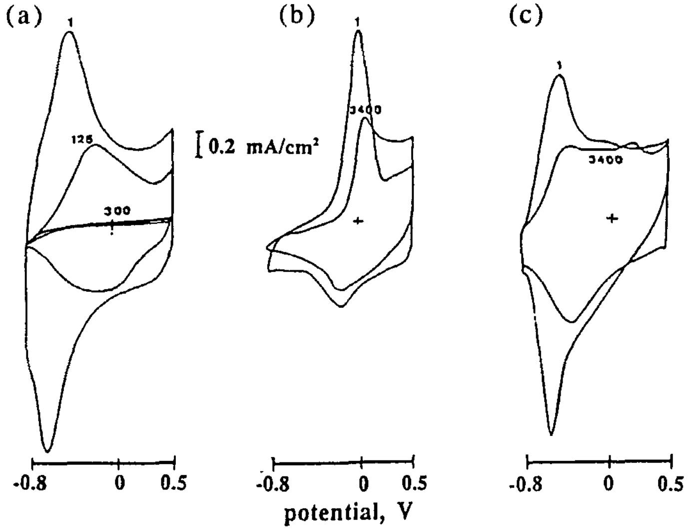

Figure 8 Electrochemical stability of PPy films in different solutions: (a) TBADS/AN system, (b) TBADS/water system and (c) NaDS/water system.

CONCLUSION

EDS and CV results suggest that when bulky DS anion is incorporated in the PPy films, the electrochemical properties are primarily determined by the electrolysis solvent. Depending on the solvent, charge-compensating ions in the polymer could be either cations in the solution or anions incorporated in the film. When the film was cycled in AN, the initial redox reaction cycle showed the sharpest peak due to free movement of DS anion in the swollen PPy film. DS anions are also involved in redox reaction in the TBADS/water solution although the redox reactivity drops significantly. However, Na cations are involved in the reaction in the NaDS/water solution. When a small Na cation is involved in balancing the charge in the polymer bulk, the relatively thick PPy behaved like a film in a thin layer cell.

Electrochemical cyclability represented by changes in the peak current with the cycle time is dependent more on electrolysis solvent or electrolyte rather than the solvent and the electrolyte used in the polymerization. In the aqueous solutions redox reactivity of the polymer was maintained even after 3400 cycles. However, in AN the reactivity did not last long due to the collapse of PPy upon removal of DS anion during cycling.

REFERENCES

1. A. F. Diaz and J. I. Castillo, J. Chem. Soc., Chem. Commun., 397 (1980).
2. M. Salmon, A. F. Diaz, A. J. Logan, M. Krounbi and J. Bargon, Mol. Cryst. Liq. Cryst., 83, 1297 (1983).
3. A F. Diaz and K. K. Kanazawa, in Extended Linear Chain Compounds, edited by J. S. Miller (Vol. 3, Plenum Press, N.Y., 1981), p.417.
4. A. F. Diaz, Chemica Scripta, 17, 145 (1981).
5. G. B. Street, in Handbook of Conducting Polymers, edited by T. A. Skotheim (Vol 1, Marcel Dekker, N.Y. and Basel, 1986), p.265 .
6. K. Kaneto and K. Yoshino, Kino Zairyo(Japan), 4, 8 (1984).
7. T. Kobayashi, H.Yoneyama and H. Tamura, J. Electroanal. Chem., 177, 281 (1984).
8. R. S. Potember, R. C. Hoffmann, H. S. Hu, J. E. Cocchiaro, C. A. Viands and T. O. Poehler, Polymer J., 147 (1987).
9. F. B. Kaufmann, A. H. Schroeder, E. M. Engler, S. R. Kramer and J. Q. Chambers, J. Am. Chem. Soc., 102(2), 483(1980).
10. J. B. Schlenoff and C. W. Chien, J. Am. Chem. Soc., 109(21), 6269 (1987).
11. A. F. Diaz, J. I. Castillo, J. A. Logan and W.-Y. Lee, J. Electroanal. Chem., 129, 115 (1981).
12. T. Iyoda, A. Ohtani, T. Shimidzu and K. Honda, Synth. Met., 18, 747 (1987).
13. T. Shimidzu, A. Ohtani, T. Iyoda and K. Honda, J. Electrochem. Soc., 224, 123 (1987).
14. Q.-Z. Zhou, C. J. Kolaskie and L. L. Miller, J. Electroanal. Chem., 223, 283 (1987).
15. J. M. Ko, H. W. Rhee, S.-M. Park and C. Y. Kim, J. Electrochem. Soc., 137(3), 905 (1990).
16. C. Y. Kim, H. W. Rhee and K. S. Min, Republic of Korea Patent Appl. 18889 (1990).
17. D.T.Sawyer and J.L.Roberts, Jr., Experimental Electrochemistry For Chemists (John Wiley & Sons, N.Y., 1974), p. 174.
18. J.M.Ko, H.W.Rhee and C.Y.Kim, Makromol. Chem., Macromol. Symp., 33, 353 (1990).