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Electrochemical Preparation, Redox Behaviour and Stability of Some Electroactive Films Having Organic/ Organic and Organic/Inorganic Hybrid Structures

AL-NAKIB CHOWDHURY* and MOSHARREFA AKTER
Department of Chemistry, Bangladesh University of Engineering and Technology
Dhaka-1000, Bangladesh
E-mail: nakib@chem.buet.ac.bd

Electrochemical polymerization of aniline from the electrolytic solutions containing (i) organic dyes, *viz.*, methylene blue or procion red and (ii) inorganic oxide, TiO_2 leads to the formation of stand-alone electroactive polyaniline/methylene blue, polyaniline/procion red and polyaniline/TiO_2 composite films, respectively. The presence of methylene blue, procion red and TiO_2 significantly affects the rate of formation, morphology and the redox activity of the composite films. The electrochemical stability of the film at highly positive potential was also examined. The results based on cyclic voltammograms demonstrate that although overoxidative degradation takes place with the composite films, the extent of degradation is not as drastic as happened with the bulk polymer film suggesting a better electrochemical stability of the composite film relative to the bulk polyaniline one.

Key Words: Polyaniline, Organic dye, Electroactive composite film, Redox activity, Electrochemical degradation.

INTRODUCTION

Polyaniline (PANI) is important conducting polymer because of its unique electronic, electrochemical and optical properties[1]. PANI can be prepared by casting the film onto an electrode surface using radio-frequency plasma[2] and electrochemical polymerization[3]. Among these, electrochemical means proves to be particularly attractive since the polymer films thus deposited electrochemically are homogeneous, adhere strongly to electrode surface. Moreover, they can be reproduced from one experiment to the next very easily. The most interesting aspect of this polymer is that it can be reversibly switched between electrochemically insulating and electrochemically conducting states by electrochemical dedoping and doping processes, respectively. Numerous studies from a variety of different fields of science have already been appeared on this insulator/conductor transition[4]. In addition to being an interesting scientific phenomenon, this switching process plays an integral role in nearly all of the proposed practical applications of electronically conductive PANI[5]. Although these materials are recognized to be highly promising for technological applications, their intractable and unprocessable nature and lack of superior environmental and electrochemical stabilities made their practical utilization limited. Several polymeric films were tested as active electrode material: PANI[6], polypyrrole (PP)[7] and polythiophene (PT)[8]. However, their electrochemical activity and stability are not necessarily enough to use them as electrode under condition required[9-11] for practical utilization. Thus, it should be important to explore active and stable polymer film coated electrodes practically available for potential use.

Preparation of composites of conducting polymers could be a potential solution to the improvement of material properties with desirable physicochemical, mechanical and electrochemical characteristics. Composite film of conducting polymer provides an attractive way of confining various chemically important species to the effective spatial region of the polymer matrices and thus offers experimental advantages of various processes to be occurred onto its surface. Platinum particles dispersed into conducting polymers (PANI, PP, PT and also their derivatives) films have been recognized as an effective electrocatalyst with high activity for the anodic oxidation of hydrogen or small organic molecules such as methanol, methanal, formic acid, etc.[12-14] Incorporating plastic or rubber with a conducting polymer is a promising method to introduce flexibility and toughness into conducting polymer, especially for PANI for which preparation of a freestanding film requires much efforts[15].

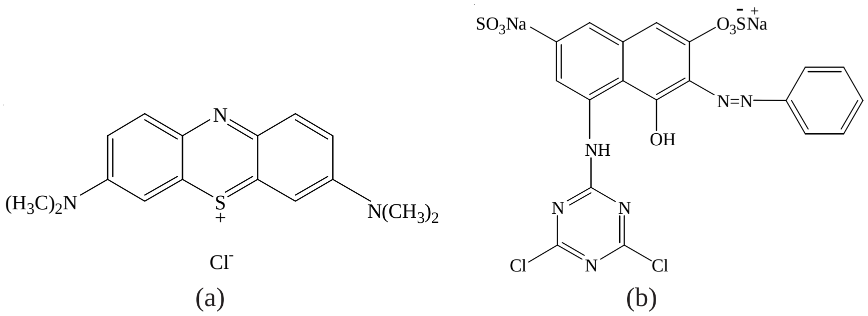
In this article, we report electrochemical preparation of some composite electrodes based on organic/organic and organic/inorganic hybrid structures. Their basic redox behaviours, stability and the extent of degradation in the electrochemical processes were also examined.

EXPERIMENTAL

Analytical grade chemicals (purchased either from E. Merck, Germany or BDH Ltd., England) were used as received except for aniline that was distilled twice prior to its use. Doubly distilled water was used as solvent to prepare all the solutions utilized in the present work.

All electrochemical experiments were performed with a potentiostat/galvanostat (Hokuto Denko, HABF 501, Japan) using a single compartment glass cell with three electrode configuration. The working electrode was a Pt foil (electrode geometric area: 0.25 cm^2). Another Pt foil and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. All potentials in the paper were presented in the SCE scale. The working electrode was carefully polished with fine-grained abrasive paper followed by cleaning several times by potential cycling between

- 0.3 and 1.0 V at 100 mV s^{-1} in 0.8 M H_2SO_4 solution. PANI film was prepared onto the Pt working electrode by sweeping the potential between -0.3 and 1.0 V at 100 mV s^{-1} from an electrolytic solution containing 0.5M aniline + 0.8 M H_2SO_4. The preparation of composite films having organic/ organic hybrid structure involves the electrolytic solutions of 1.93×10^{-5} M methylene blue (MB) + 0.5 M aniline + 0.8 M H_2SO_4 and 1.93×10^{-5} M procion red (PR) + 0.5 M aniline + 0.8 M H_2SO_4 to form PANI/MB and PANI/PR films, respectively. These films were also deposited onto the Pt electrode by sweeping the potentials between - 0.3 and 1.0 V at 100 mV s^{-1} from their respective electrolytic solution. MB is cationic in nature while PR is an anionic one. The chemical structures of MB and PR are presented in **Scheme-1**. On the other hand, preparation of composites film having organic/ inorganic hybrid structure employed an electrolytic solution containing a suspension of TiO_2 (0.5 g TiO_2 in 400 mL distilled water) + 0.5 M aniline + 0.8 M H_2SO_4. PANI/TiO_2 film was deposited onto Pt substrate by potential sweeping between - 0.2 and +1.0 V at 100 mV s^{-1} in the electrolytic solution. After preparation, all the films as coated onto the Pt electrodes were washed several times with 0.8 M H_2SO_4 solution to remove any traces of electrolytic solution, or by-products that might produce during polymerization.



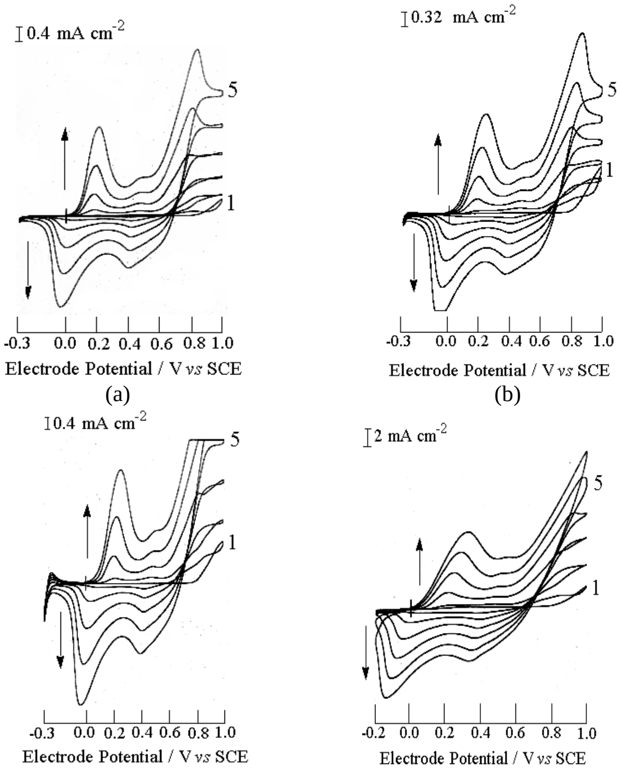
(a) (b)

Scheme-1 Chemical structures of (a) MB and (b) PR

A scanning electron microscope (SEM) (Philips XL 30) was used to examine the morphology of the PANI and composite films. The film coated Pt substrate was fixed on the sample holder using an electroconductive adhesive and then a thin layer of gold about 400 Å in thickness was sputtered onto the film in order to improve the SEM image resolution. Density measurement of the samples was carried out in a pycnometer (Micromeritics Multivolume Auto Pycnometer, model no. 1305, USA) following the conventional standard method. Two-point probe method was employed for measuring compressed pellet d.c. conductance of PANI and the composite samples. Resistance for each sample could read directly from an auto ranging microvolt (Keithley 197A, USA) equipment and thus specific conductance of the sample was calculated out. All the experiments in this work were conducted at room temperature (28 ± 1ºC).

RESULTS AND DISCUSSION

Electrochemical preparations of PANI, PANI/MB, PANI/PR and PANI/ TiO_2 films were carried out by anodic oxidation of aniline onto the Pt substrates from the respective electrolytic solutions as described in the experimental section. Typical cyclic voltammograms (CV's) during synthesis of these films are shown in Fig. 1. In all the CV's depicted, the common features are: on sweeping the first potential cycle from - 0.3 to 1.0 V, a sharp rise in current is seen at potential *ca*. 0.8 V indicating the oxidation of aniline to yield PANI[16]. A thin deep blue film was seen to be adhering onto the Pt surface. As the sweeping repeated, *i.e.*, in the second and subsequent cycles, the peak current increases further indicating the formation of more deposits of film onto the surface. The anodic peak at *ca*. 0.18 V is seen to observed from the second scan. This peak can be assigned to the oxidation of PANI film corresponding to the conversion of amine units to radical cations in the polymer chain[17]. However, the CV's for PANI/MB and PANI/ PR show additional peaks at *ca*. - 0.3 V. This peak is not observed when the film is prepared in absence of either of MB or PR dye solution in the electrolytic media. Thus, the redox response as observed at *ca*. - 0.3 V may arise only if either of the film or the electrolytic solution contains the dye. In case of the PANI/TiO_2, no additional peak is observed in the CV. Indeed, TiO_2 is electrochemically stable at least the potential window (-0.3 to 1.0 V) employed for sweeping in this experiment. The above results of CV during electrochemical preparations of PANI, PANI/MB, PANI/PR and PANI/ TiO_2 films clearly indicate that the matrices are capable of performing redox processes onto their surfaces. The redox activity of the films are evaluated from their corresponding CV (Fig. 1) as follows: from the 5th cycle of potential scan under polarization between -0.3 and 1.0 V, the first anodic (I_{pa}) and corresponding cathodic (I_{pc}) peak currents appear at potential E_{pa} and E_{pc}, respectively, were found out and the data are presented in Table-1. From the data, it seems that the redox reactivity of the matrices varies considerably. Peak separation between E_{pa} and E_{pc} and the ratio, I_{pc} to I_{pa} are considered for the measure of reversibility. The difference of the reversibility (Table-1) of the film electrodes prepared may suggest that redox process onto their surfaces proceeded not in a similar fashion and thus show dissimilar redox reactivity of the film electrodes. This could be realizable if one considers modification of the PANI surface that might happen by the incorporation the MB, PR and TiO_2 in the polymer matrix. The densities of PANI, PANI/MB, PANI/PR and PANI/TiO_2 samples were measured to be 1.42, 1.46, 1.49 and 1.58 g cm^{-3}, respectively. The observed higher densities for the composites samples than that of the PANI may support the incorporation of MB, PR and TiO_2 particles into the polymer matrix during its synthesis.



(a) (b)

(c) (d)

Fig. 1 CV's during electrochemical synthesis of (a) PANI, (b) PANI/MB, (c) PANI/PR and (d) PANI/TiO_2 films

Attempt was also made to get insight about the rate of polymerization of aniline in the absence and presence of MB, PR and TiO_2. It was reported[18,19] that the mass and thickness of the PANI film formed onto the substrate are proportional to the anodic peak current, I_{pa} at *ca.* 0.17 V. Therefore, the rate of polymerization can be measured by the rate of increase in this peak current. Fig. 2 shows a typical plot of I_{pa} therefore, the amount of film formed on the Pt electrode against the number of cycles (*i.e.*, the reaction time, t) obtained from the CV's (Fig. 1) for the preparation of the PANI, PANI/MB, PANI/PR and PANI/TiO_2 films. The slope, $d(I_{pa})/dt$, at any points of these curves, gives the rate of polymerization at the corresponding reaction time. It is apparent in Fig. 2 that the growth of the films onto the Pt surfaces is affected significantly by the presence of MB, PR or TiO_2 in the electrolytic media. The growth rates seem to be faster for PANI/TiO_2 and PANI/PR films than that of PANI whereas it decreases for the growth of PANI/MB film. The reason of this finding is yet to be understood, however, it may be assume that the addition of TiO_2 and PR in the electrolytic media may facilities the slow step of the polymerization resulting in the increase in overall rate of polymerization. On the other hand, the slower growth rate that observed with other system may result from the inhibition of nucleation species on which the polymer chain grows[18-21].

TABLE-1
REDOX REACTIVITY OF DIFFERENT ELECTRODE MATRICES

Electrode matrix	Anodic peak current, I_{pa} (mA cm^{-2})	Anodic peak potential, E_{pa} (V)	Cathodic peak potential, E_{pc} (V)	Cathodic peak current, I_{pc} (mA cm^{-2})	I_{pc}/I_{pa}
PANI	2.32	+0.19	-0.03	1.52	0.655
PANI/MB	1.38	+0.21	-0.05	1.56	1.130
PANI/PR	3.28	+0.26	-0.04	3.60	1.097
PANI/TiO_2	5.80	+0.28	-0.12	6.80	1.172

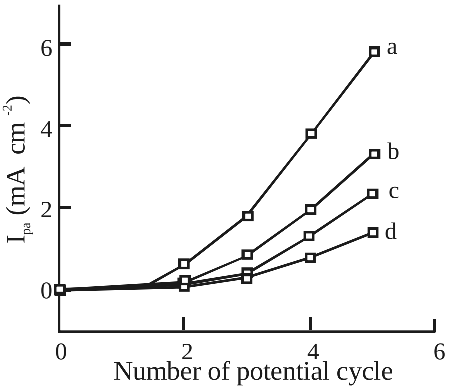


Fig. 2. Dependence of anodic peak current densities (at *ca.* 0.17 V) on the cycle number during electrochemical synthesis of (a) PANI, (b) PANI/MB, (c) PANI/PR and (d) PANI/TiO_2 films

Composition and morphological structure of a material strongly depends on the mode of synthesis, be it chemical or electrochemical, on the synthesis conditions, chemical nature of the reactants and products etc. Thus, there is a variety of chemical structure and morphology of a material is possible. In the present work, various chemical entities, *viz.*, MB, PR and TiO_2 were attempted to embed into the PANI films during their electrochemical synthesis. In order to examine the surface morphologies of these films, SEM analysis was adopted. Fig. 3 shows the SEM micrographs of (a) PANI, (b) PANI/MB, (c) PANI/PR and (d) PANI/TiO_2 films. A grain-like morphology is seen for the PANI film. The PANI grains seem to be uniformly distributed over the substrate. The surface morphology of the PANI/MB seems also to be granular, however, some grains are assembled to a bigger particle and distributed less uniformly on the surface. On the other hand, PANI/PR surface seems to be composed of short fibrils and distributed randomly onto the substrate. The PANI/TiO_2 shows a compact aggregation of the deposit in a long stack. The deposit in the stack seems to be relative tightly packed to form a rigid body that distributed non-uniformly over the substrate. The present SEM observation clearly demonstrates a dissimilar surface morphology of the PANI films. This might occurred due to incorporation of the MB, PR and TiO_2 species into the PANI matrix. Modification of the PANI surface is also reported by the early workers[22-24] by varying synthesis condition. From the observed dissimilar morphological features of PANI, PANI/MB, PANI/PR and PANI/TiO_2 films, it is expected that their electrode behaviour for electrochemical processes could be different. The redox behaviours of these films are, indeed found to proceed in a dissimilar fashion as described earlier in the text.

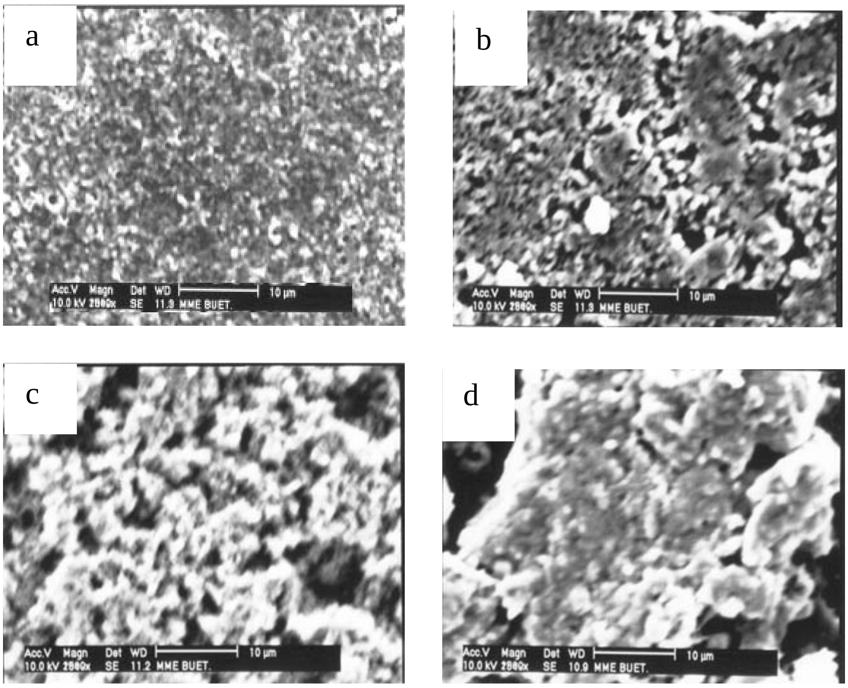
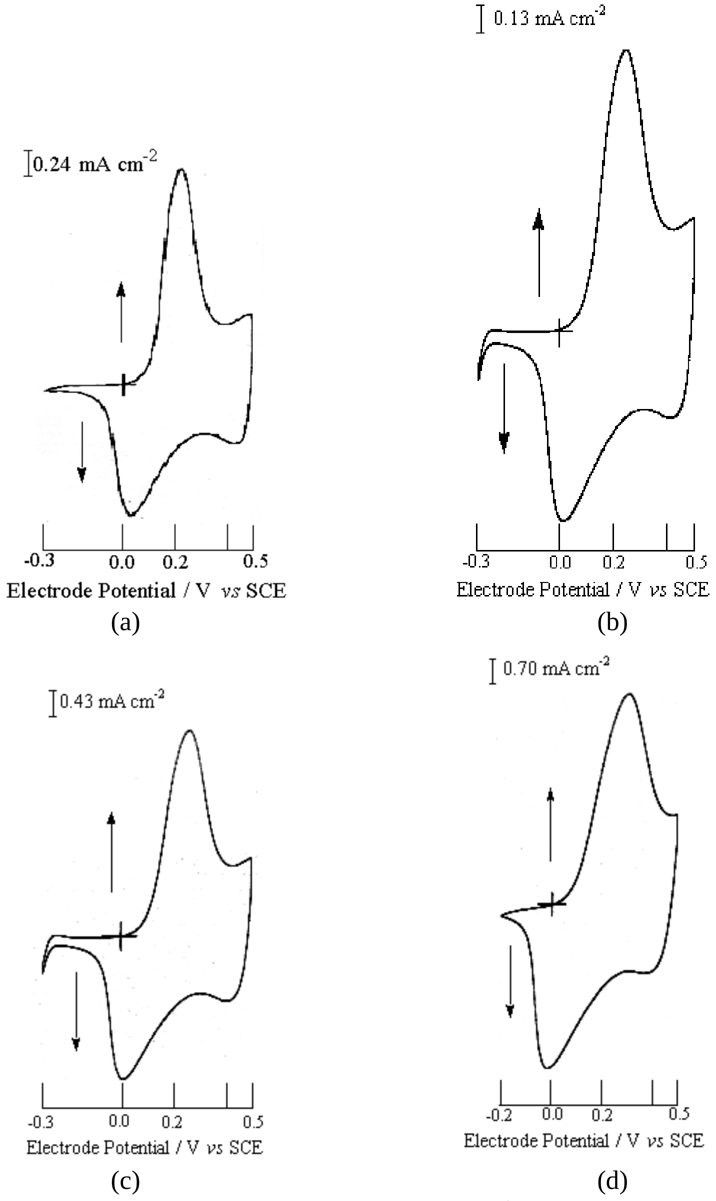


Fig. 3. SEM micrographs of (a) PANI, (b) PANI/MB, (c) PANI/PR and (d) PANI/TiO_2 films

Compressed pellet d.c. conductivities of the sample PANI, PANI/MB, PANI/PR and PANI/TiO_2 measured by a conventional two-point probe method were found to be 3.11×10^{-1}, 1.92×10^{-1}, 5.18×10^{-1} and 9.63×10^{-1} S cm^{-1}, respectively. The entities embedded into the PANI matrix have dissimilar chemical nature, *viz.*, MB is cationic and PR is anionic, while

TiO_2 is semiconducting in nature. The presence of the embedded entities (having different chemical nature) into the PANI matrix may play certain role in modifying the electrical conductance of the matrices. The change in electrical conductivity is also reported by the early workers[25,26] for surfactant incorporated conducting polymers. However, it is worth noticing that the conductivities of the composites matrices thus prepared in the present study, correspond to the range of conventional semiconductor conductivity and therefore, the result may suggest the possibility of using the composites as electroactive film electrode in the electrochemical processes.

The electrochemical doping-dedoping (oxidation-reduction) behaviours of the film matrices were examined by cyclic voltammetry in aqueous 0.8 M H_2SO_4 electrolytic solution. Typical CV's of (a) PANI, (b) PANI/MB, (c) PANI/PR and (d) PANI/TiO_2 films are shown in Fig. 4. The CV of PANI shows clearly one well-defined peak at *ca*. 0.2 V in the anodic sweeping while in its cathodic scan, a peak appears at *ca*. 0.04 V, suggesting the presence of electroactive region in the film[27,28]. The peak at 0.2 V indicates the oxidation of PANI at which electrolytic anion (SO_4^{2-}) doped into the polymer film. The PANI film reduced at 0.04 V where dedoping of the SO_4^{2-} anion occurred. The redox process was accompanied by colour change. The film appears to be deep blue when the electrode potential was positive of 0.2 V and turns to greenish-yellow on switching the potential a negative of -0.2 V. Similar observation for color changes with PANI in its redox process was also reported previously[3(a),29]. Alike PANI film, the results in Fig. 4 also show that the composite films PANI/MB, PANI/PR and PANI/TiO_2 can be switched between their oxidized and reduced states with concomitant color changes and thus indicates the presence electroactive region in the composites films. It is, therefore, evident that even after incorporating MB, PR and TiO_2 into the PANI matrix, the resulting composite films exhibit excellent electroactivity comparable to that of unique conducting polymers, *viz.*, PANI, PP and PT films. However, the CV's of PANI/MB and PANI/PR show additional redox process in the region *ca*. - 0.3 V. Similar redox process was also observed when PANI was synthesized from an electrolytic solution containing either of MB or PR in the media (Fig. 1). In this case (Fig. 4), the electrolytic media is free from MB or PR. Thus, redox response could be the contribution of MB or PR that might have incorporated into the polymer matrix during its synthesis. It can be seen from the result that no additional response in the CV of PANI/TiO_2 film is observed. This may be due to the fact that TiO_2 is electroinactive with in the potential window scanned.

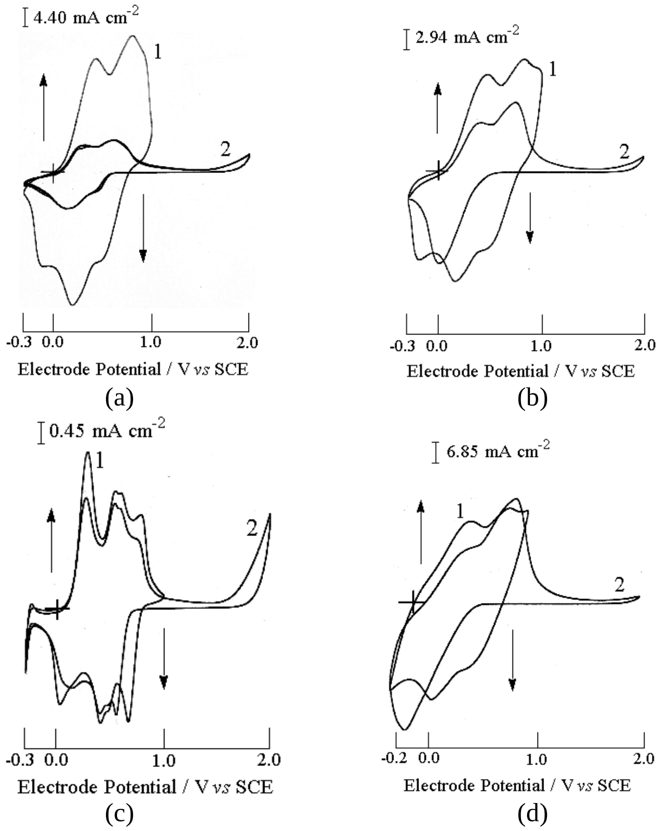


(a) (b)

(c) (d)

Fig. 4. CV's during doping-dedoping processes of (a) PANI, (b) PANI/MB, (c) PANI/PR and (d) PANI/TiO_2 film electrodes

The stability of PANI and the composites films in highly positive potential were also examined. Fig. 5 shows the CV's of (a) PANI (b) PANI/MB (c) PANI/PR and (d) PANI/TiO_2 films in 0.8 M H_2SO_4 solution. It can be seen from the voltammogram (curve-1, Fig. 4a) that the PANI film gives a normal reversible redox response when the potential scan was reversed at a switching potential of 1.0 V. However, when the scan was reversed at a more positive potential of 2.0 V (curve-2, Fig. 4a), normal redox phenomenon seems to be affected significantly, for example, the peaks observed in the curve-2 becomes broader, peak positions are shifted and also the peak intensities are reduced significantly. Thus, electroactive nature as indicated by redox peaks in curve-1 seems to be destroyed. This phenomenon is called overoxidative degradation and is found in some kind of conducting polymers such as PANI, PP and PT[9-11]. Similar study was carried out with PANI/MB, PANI/PR and PANI/TiO_2 films and the results are depicted in Fig. 5(b-d). The redox response of the films under potential of 1.0 V (curve-1) and 2.0 V (curve-2) seems to be nearly identical. From the results, it appears that although overoxidation takes place with the composite films, the extent of degradation is not as drastic as happened with PANI one. Overoxidative degradation may be rationalized as due to the formation of dications of aniline moieties in the PANI film. The dication should be very strong electrophiles and easily undergo nucleophilic attack with successive decomposition[9].



(a) (b) (c) (d)

Fig. 5. CV's of (a) PANI, (b) PANI/MB, (c) PANI/PR and (d) PANI/TiO_2 film electrodes in 0.8 M H_2SO_4 solution: 1.0 V (curve-1) and 2.0 V (curve-2)

Conclusion

In summary, a simple route for the preparation of free-standing composites films, *viz.*, PANI/MB, PANI/PR and PANI/TiO_2 by electrochemical polymerization of aniline from the electrolytic solution containing MB, PR, and TiO_2, respectively is described. The composite films thus synthesized exhibit excellent electroactivity that comparable to that of the bulk polymer. The electrochemical degradation observed with the composite films seems to be less drastic compared to that of PANI film and hence offer a relatively superior electrochemical stability for the PANI/MB, PANI/PR and PANI/TiO_2 films over the bulk PANI one.

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