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Preparation and electroactivity of polyaniline /poly(acrylic acid) film electrodes modified by platinum microparticles

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The preparation and properties of poly(acrylic acid) (PAA)-doped polyaniline (PANI) film electrodes further modified by electrodeposition of platinum particles were investigated by cyclic voltammetry and *in situ* conductivity measurement. The PANI/PAA film exhibits a better electroactivity and higher stability, even in solutions of lower acidity, although its polymerization rate is decreased threefold compared to that of PANI. The conductivity of the PANI/PAA film increases by a factor of two compared to that of PANI. The effects of the carboxylic acid groups of PAA in the PANI matrix on the performance of the film are discussed. The electrocatalytic activity of PANI/PAA/Pt for reduction of hydrogen and oxidation of MeOH is higher than that of PANI modified with Pt particles alone. Characterization of the electrodes by SEM shows the platinum modification procedure yields roughly spherical catalyst particles 0.5–1 μm in diameter dispersed throughout the polyaniline.

Keywords: *polyaniline*, *poly*(*acrylic acid*), *platinum microparticles*, *conductivity*, *electrocatalysis*

1. Introduction

Conducting polymer films are often utilized for the fabrication of functionalization electrodes having molecular selectivity [1–3] and electrocatalysis [4–6]. The polymeric acid has been used as a template [7, 8] for the oxidative polymerization of aniline. The incorporated polyanions in the polymer matrix are not released due to its huge molecular volume and electrostatic interaction with the positive charge of PANI chains. Therefore, its properties are different from that of small molecular acid-doped PANI. A series of polymeric acids has been used as dopants, such as poly(styrenesulfonic acid) [9–12], poly(acrylic acid) [13, 14], poly(ethenesulfonic acid) [14] and poly (methacrylic acid) [15].

Metal particles dispersed into conducting polymer films have been recognized as effective electrocatalysts with high activity for various electrode reactions. PANI/Pt modified electrodes have been studied for the oxidation of methanol [16] and formic acid [17], PANI/Pd assemblies [18, 19] and polypyrrole/Pt [20] for H_2 oxidation and O_2 reduction, polythiophene/Pt for formic acid oxidation [21], poly(3-methyl thiophene)/Pt–Sn for MeOH oxidation [22] etc.

This work was undertaken to study the fabrication and electrochemical behaviour of PAA-doped PANI film. The electrocatalytic responses of PANI/PAA films modified with platinum particles were also investigated for reduction of hydrogen and oxidation of MeOH in acidic aqueous solutions.

2. Experimental details

Aniline was purified by repeated distillation with zinc dust and stored under nitrogen gas. All other reagents were of analytical grade and were used as-received. All the solutions were prepared with twice distilled water.

The electrochemical experiments were performed in a three-electrode cell, using a platinum disc working electrode of 6 mm diameter, a platinum sheet counter electrode and a saturated calomel electrode (SCE) as reference at room temperature under nitrogen atmosphere. The working electrode was polished mechanically using emery paper (grade 800) to a mirror surface and then cleaned by potential cycling between −0.2 and 1.2 V at 50 mV s^{-1} in 0.5 M H_2SO_4 until a stable voltammogram was obtained.

The PANI/PAA film was formed by cyclic voltammetry at 50 mV s^{-1} between −0.2 V and +0.9 V vs SCE for about 20 min in solutions of 0.1 M aniline and 0.5 M H_2SO_4 containing 1% PAA (with a viscosity-average molecular weight of 800 000). The platinum modification was performed by potentiodynamic cycling at 50 mV s^{-1} between −0.2 and +0.5 V vs SCE in 0.5 M H_2SO_4 containing 2 mM K_2PtCl_6.

Electrocatalytic oxidation of methanol on PANI or PANI/PAA films containing dispersed Pt particles was examined in 1 M MeOH/0.5 M H_2SO_4 solution by

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cyclic voltammetry at 50 mV s^{-1} between −0.2 and +0.65 V.

Cyclic voltammetry was performed using a bipotentiostat/galvanostat (EG&G, model 366) and recorded on an X–Y recorder (EG&G, model RE0150). *In situ* conductivities of polymer films were measured using the four-microprobe method [23]. The SEM experiments were made on a Hitachi X-650 scanning electron microanalyser.

3. Results and discussion

3.1. *Preparation and electrochemical behaviour of PANI/PAA film electrode*

Figure 1 shows cyclic voltammograms recorded during electropolymerization of PANI/PAA film. The first cycle shows a ‘nucleation-loop’ due to aniline monomer oxidation and film formation. During the following cycles, the redox currents gradually increase, and a series of new oxidation peaks is observed at 0.19, 0.45 and 0.71 V. The polymerization rate falls by a factor of three in comparison with that of PANI in the absence of PAA. This means that the large polyanions have been incorporated into the PANI matrix and then impede the effective doping of small molecular anions in the electrolyte. The cyclic voltammogram of PANI/PAA film in 0.5 M H_2SO_4 is shown in Fig. 2. The second reduction peak (E_{p-2}) is very sharp, and two pairs of reversible redox peaks are observed at 0.19/0.07 V and 0.71/0.69 V, respectively, which are closer to each other in that the first oxidation peak (E_{p+1}) is positively shifted by 30 mV and the second oxidation peak (E_{p+2}) is negatively shifted by 50 mV compared to those observed in PANI film undoped by PAA. This has also been observed in substituted polyaniline [24] and is associated with the steric and electronic effects of the substituents. In the film of PANI/PAA, the carboxylic acid groups of PAA have a strong electrostatic interaction with cationic radicals along the PANI backbone and a hydrogen bonding effect with the amine of the PANI chain. Thus, a higher potential for the formation of a polysemiquinone radical cation (E_{p+1}) is required, while the polysemiquinone oxidation associated with deprotonation occurs more easily, leading to a lower potential for the second oxidation process(E_{p+2}). The generated protons may combine with the counterion (–COO^-), to yield –COOH.

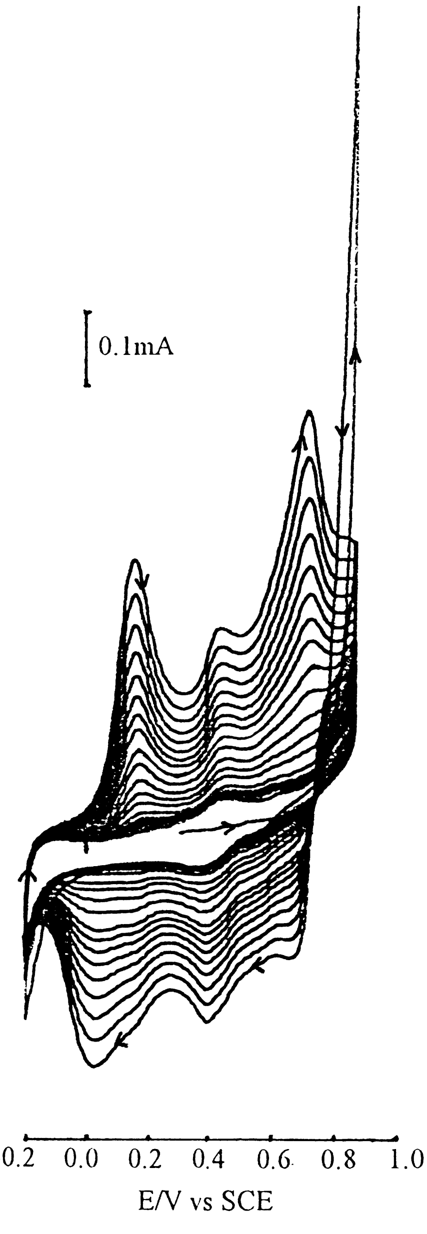

Fig. 1. Cyclic voltammograms during polymerization in 0.5 M H_2SO_4 solution containing 0.1 M aniline and 1% PAA at a sweep rate of 50 mV s^{-1}.

3.2. *Effect of pH on PANI/PAA film electrode*

Cyclic voltammograms (CVs) of PANI/PAA in saturated K_2SO_4 solution at different pH adjusted by 0.5 M H_2SO_4 and 0.1 M NaOH solutions are shown in Fig. 3, and the peak potential–pH dependence of the

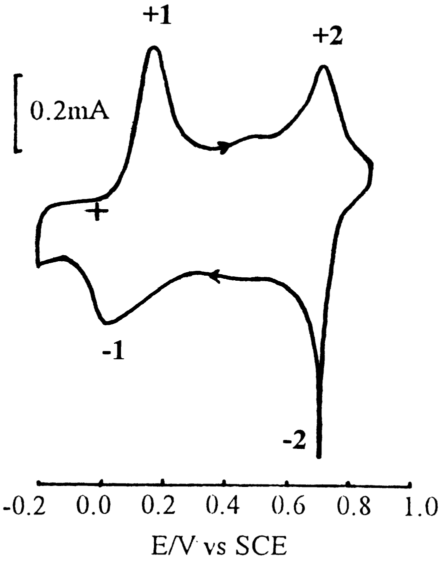

Fig. 2. Cyclic voltammogram of PANI/PAA film ($d = 93$ nm) prepared as in Fig. 1 in 0.5 M H_2SO_4 at 50 mV s^{-1}.

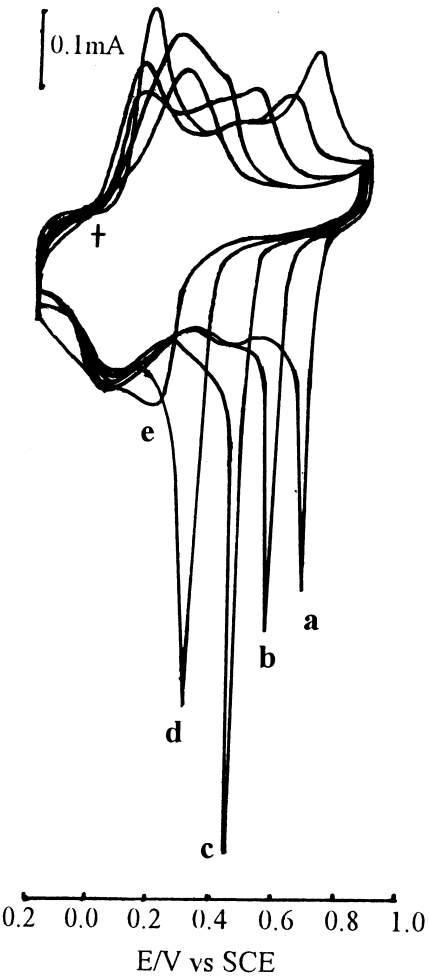

Fig. 3. Cyclic voltammograms of PANI/PAA film ($d = 66$ nm) in saturated K_2SO_4 solutions at different pH values: (a) 0, (b) 1.1, (c) 2.1, (d) 3 and (e) 4. Sweep rate 50 mV s^{-1}.

PANI/PAA film electrode is shown in Fig. 4. The results show that the E_{p+1} does not change at pH $0 \sim 2$, indicating only the loss of electrons for the first peak; but the E_{p+2} and E_{p-1} vary linearly with pH at a slope of −110 mV/pH. This is consistent with a two-proton per electron process as observed in the PANI film [25]. When pH > 2, the E_{p+1} shifts positively, implying that the stronger interaction between the carboxylic groups of the PAA and the PANI chain causes the localization of charges and reduces the stability of the polysemiquinone radical cations. Otherwise, the second reduction peak (E_{p-z}) of the CVs is very sharp at pH 2. This may be related to the proton-exchange reaction and the redoped process between the carboxylic acid groups of PAA and the PANI chains. The pK_a of acrylic acid is 4.25 while the value for PAA must be larger due to the electronic effects of the long chains. PAA is partially ionized in 0.5 M H_2SO_4 (pH ~ 0). The degree of ionization and deprotonation of PAA increases with increasing pH. Generally, the PANI film exhibits electroactivity only in acidic solution. Many efforts have been made to extend the electroactivity to higher pH [26]. Here, when the pH rises to 4, a pair of redox peaks is still observed and the PANI/PAA film maintains good electroactivity. This is attributed to the local acidity and ionic conductivity of PAA, as well as the proton-transfer reaction between the PANI chains and carboxylic acid groups of PAA.

3.3. *In situ conductivity measurements*

Figure 5 shows the results of *in situ* conductivity measurements for PANI/PAA and PANI film. The maximum conductivity is 11.6 S cm^{-1} at 0.4 V for the PANI film and 22.1 S cm^{-1} at +0.4 V for the PANI/PAA. As can be seen, the conductivity of PANI/PAA greatly increases at the intermediate oxidation state. The electron-donating effect and the electrostatic interaction of the carboxylic acid group of PAA results in an increase in conductivity. When PANI/PAA film is in the reduced state or the highly oxidized state ($E < 0.1$ V or $E > 0.6$ V), the conductivity decreases dramatically and is even less than that observed in the PANI film. This means that radical cations of PANI/

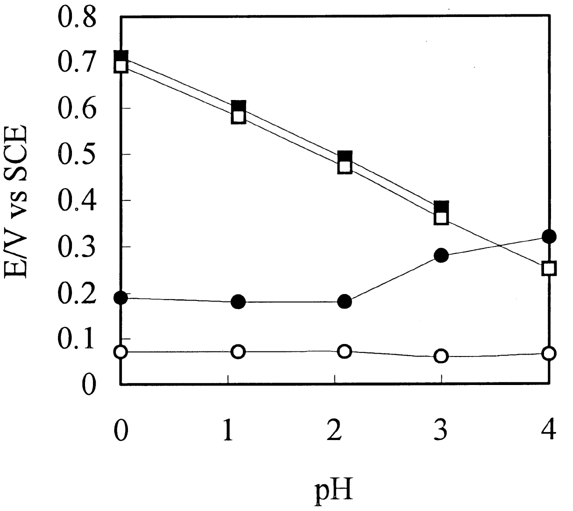

Fig. 4. The dependence of potential on pH for PANI/PAA film electrode. (Data from Fig. 3.) E_{p+1}(■)/E_{p-1}(□) the first redox process; E_{p+2}(●)/E_{p-2}(○) the second redox process.

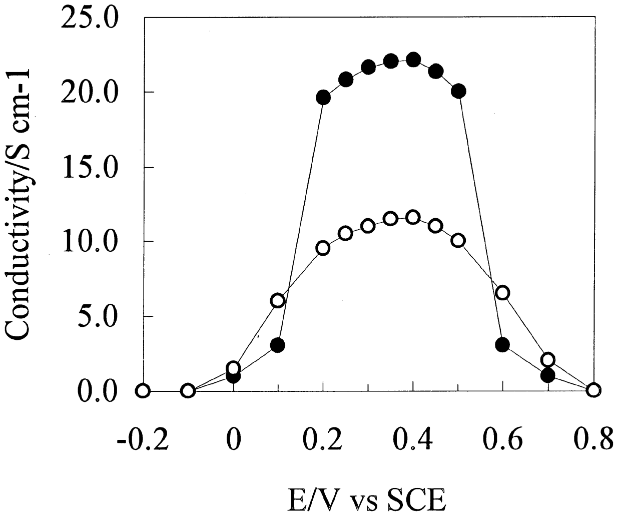

Fig. 5. Potential dependence of the conductivities for PANI/PAA film ($d = 93$ nm, ●) and PANI film ($d = 86$ nm, ○) in 0.5 M H_2SO_4 solution.

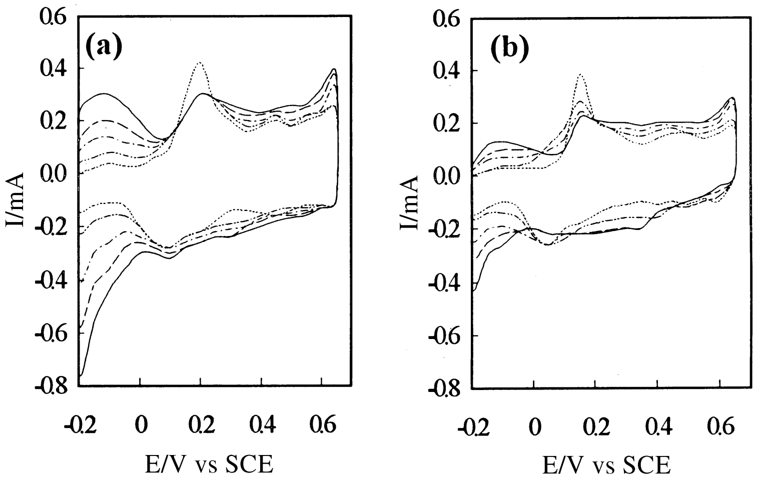

Fig. 6. Voltammograms of (a) PANI/PAA film ($d = 93$ nm) and (b) PANI film ($d = 86$ nm) modified by platinum particles in 0.5 M H_2SO_4 at 50 mV s^{-1}. Time (t_d) of platinum deposition (··········) 0; (–··–··–··) 5; (–·–·–·–) 10; (– – – –)15 and (——) 20 min.

PAA form less easily but are more easily oxidized as against those of PANI. The fewer charge carriers, that is, radical cations or polarons, lead to the lower conductivity.

3.4. *Electrocatalytic reduction of hydrogen and oxidation of methanol*

As is well known, the oxidation of methanol on bare platinum is slow; the decrease in activity with time may be attributed to C — OH strongly adsorbed on the Pt surface hindering the reaction to produce CO_2 [27]. A high conductivity of PANI/PAA films can be easily obtained in the potential range 0.15 to 0.55 V without degradation of the polymer, which facilitates charge transfer through the conductive polymer structure.

Voltammograms recorded in 0.5 M H_2SO_4 are shown in Fig. 6 for (a) PANI/PAA film and (b) PANI film modified by platinum particles at different

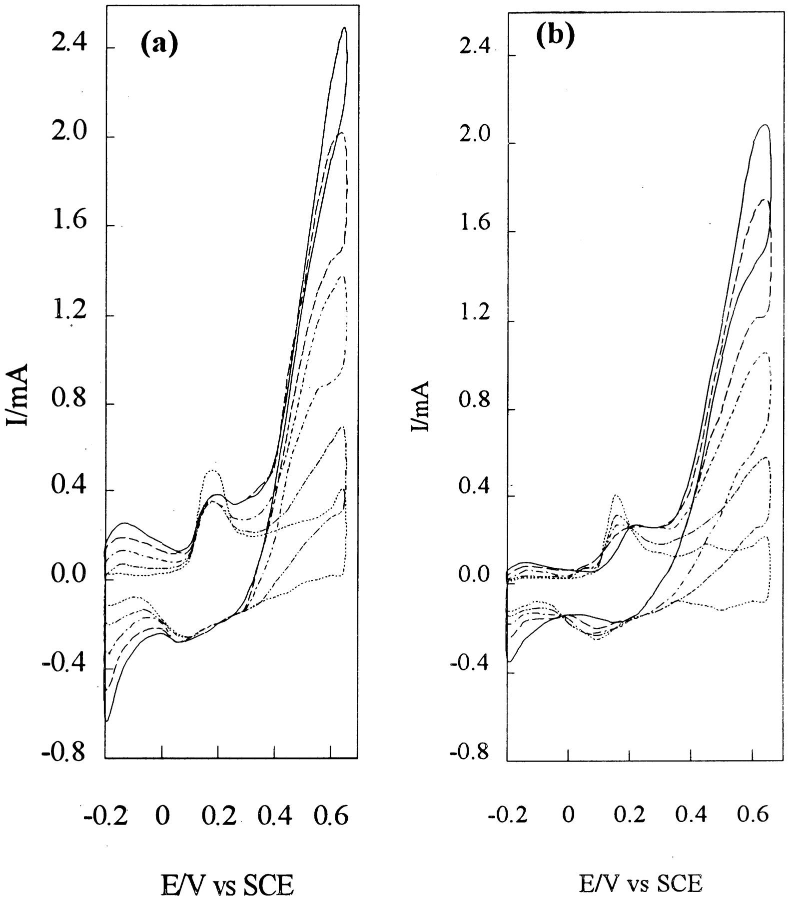

Fig. 7. Voltammograms of MeOH oxidation under the same experimental conditions as in Fig. 6 but with 1 M MeOH.

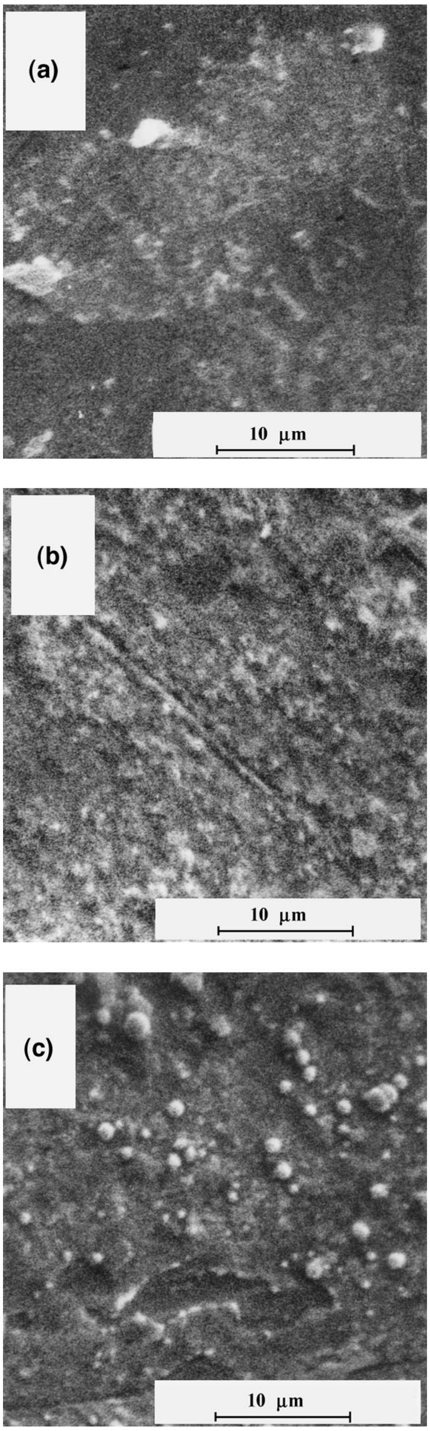

Fig. 8. SEM photographs of the modified films equilibrated at 0.4 V in 0.5 M H_2SO_4. (a) PANI ($d = 90$ nm); (b) PANI/PAA ($d = 95$ nm) (c) PANI/PAA/Pt ($t_d = 20$ min).

deposition times. For a successive Pt deposit, the reversible peaks of PANI film are inhibited, but those of PANI/PAA film still show some electroactivity. At the same conditions of Pt deposition, the catalytic currents of hydrogen at PANI/PAA/Pt are much higher than those of the PANI/Pt electrode. This indicates that the PANI/PAA/Pt film has a better electrocatalytic activity.

The voltammetric behaviour of platinum-modified polymer electrodes for electrocatalytic oxidation of MeOH is shown in Fig. 7. Smaller oxidation current is found on PANI film compared to the PANI/PAA film. This result may also be attributed to the higher conductivity and faster charge transfer of PANI/PAA film in the intermediate oxidation state. It must be pointed out that the catalytic current is greatly increased with increase in the amount of deposited Pt. It is also observed that the catalytic activity of PANI/PAA/Pt is much better than that of PANI/Pt film.

The morphology of the polymer varies with the changing nature of the counter ion. As can be seen in Fig. 8, PANI film shows a loose and granulated structure, but PANI/PAA film has a compact and well-distributed structure due to the slower polymerization rate, which exhibits a high conductivity in the intermediate state and better electroactivity. The Pt microparticles with 0.5–1 μm diameter can be clearly seen at the surface of the PANI/PAA/Pt film; these form active centres for the enhancement of electrocatalytic activity.

4. Conclusion

The electroactivity and conductivity of PANI film are greatly enhanced by doped PAA. Conductivity of PANI/PAA increases by a factor of two compared to that of PANI film at the intermediate state; however, in its reduced state and highly oxidized state, the conductivity falls dramatically. The PANI/PAA/Pt film electrode shows a higher catalytic activity for hydrogen reduction and methanol oxidation than PANI modified with Pt particles alone. The fabrication of molecular sensitive film electrodes based on such polymer–metal composite layers is an attractive prospect.

Acknowledgements

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