JOURNAL OF MATERIALS SCIENCE 32 (1997) 783–787

Effect of supporting electrolyte on the polymerization of electrochemically deposited poly(*o*-anisidine) films

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Poly(*o*-anisidine) films deposited galvanostatically exhibit the formation of different oxidation states of the polymer with varying pH of the solution. The influence of supporting electrolyte on the extent of formation of the conducting phase at pH 2.1 has been investigated with the help of optical, thermal and potential cycling techniques. The optical spectra of the films reveal the proportionate increase in the fraction of the conducting emeraldine salt phase with the amount of supporting electrolyte (NaCl) added to the solution. Similarly, clarity in the decomposition steps of the thermal patterns and redox peaks in the cyclic voltammograms are found to increase as a function of NaCl concentration.

1. Introduction

Polyaniline and its derivatives are members of the conducting class of polymers possessing potential applicability for their substantial use in technological applications [1–3]. The inability of polyaniline to dissolve in common organic solvents has restricted its utilization in certain fields [4]. This problem is overcome by incorporating a substituent at a proper position. As in polyaniline, the electro-oxidation of poly(*o*-anisidine) in aqueous acidic media yields a film with desirable properties [5]. The media in which the films are grown is an important prerequisite for achieving selectivity in the formation of a particular oxidation state of the polymer. Also, the addition of supporting electrolyte, especially in a solution containing a small amount of hydrochloric acid, is necessary to have a diffusion-controlled polymerization process. But while doing so, it is essential to ensure its role in affecting the polymerization process. Keeping this objective in mind, the present work explored the effect of the supporting electrolyte on the formation of the conducting phase of electrochemically grown poly(*o*-anisidine) films with the help of optical, thermal and potential cycling techniques.

2. Experimental procedure

All chemicals used were of AR grade. The solutions with different pH values (− 0.21, 2.1 and 4.13) were prepared by the addition of appropriate amounts of HCl in doubly distilled water. The monomer concentration was kept fixed at 0.1 M in each case. The concentration of NaCl acting as a supporting electrolyte was maintained at 1.0 M in a solution of pH 2.1 and 4.13. Three electrode systems consisting of SnO_2: F (1 cm × 1 cm, sheet resistance $10\ \Omega/\square$) as a working electrode, calomel as a reference electrode and platinum as a counter electrode, were used for polymer deposition, except that for cyclic voltammetric experiments, the size of the working electrode used was 0.3 cm × 1 cm. Galvanostatic depositions were carried out using potentiostat/galvanostat (Elico, CL-95) at a current strength of 1.0 mA. Cyclic voltammograms were recorded on Bas model (CV-27) at a scan rate of $100\ \mathrm{mV\,s^{-1}}$ by cycling the potential between − 0.2 and + 1.0 V. Optical characterization of galvanostatically deposited films was done using an Hitachi-220, ultraviolet–visible double-beam spectrophotometer. Thermograms were obtained on a Perkin–Elmer (Delta series TGA-7) instrument in an oxygen atmosphere at a scanning rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$.

3. Results and discussion

Variation in the nature of the optical spectra of poly(*o*-anisidine) films deposited as a function of the pH of the solution is shown in Fig. 1. Sharp differences in the optical spectra reveal the strong dependence of the polymerization process on the pH of the solution which governs the formation of a particular oxidation phase of the polymer. A sharp peak located at ∼ 850 nm in the optical spectra of the film deposited from a solution of pH − 0.21, indicates the preferential formation of the conducting emeraldine salt

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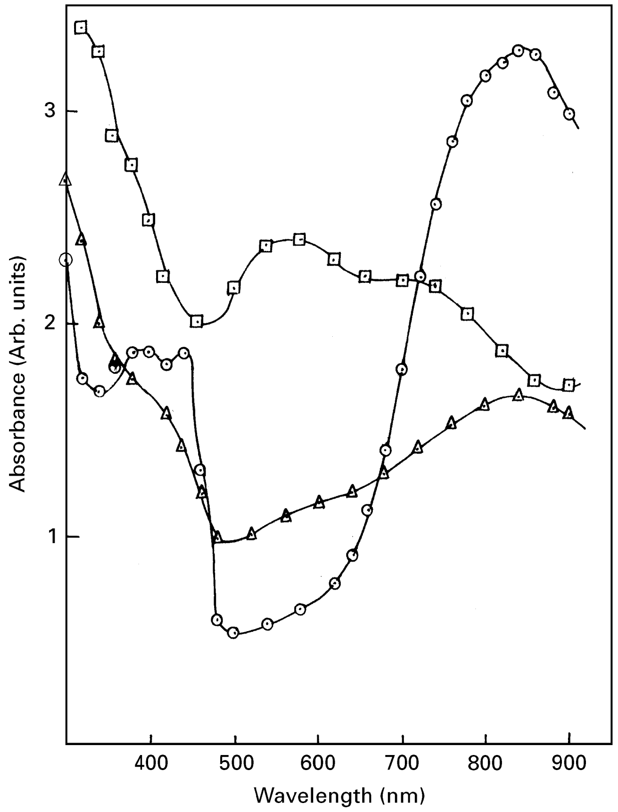

Figure 1 Absorption spectra of electrochemically deposited poly(*o*-anisidine) films as a function of pH of solution: (⊙) 0.21, (△) 2.1, (⊡) 4.13. Deposition time = 5 min.

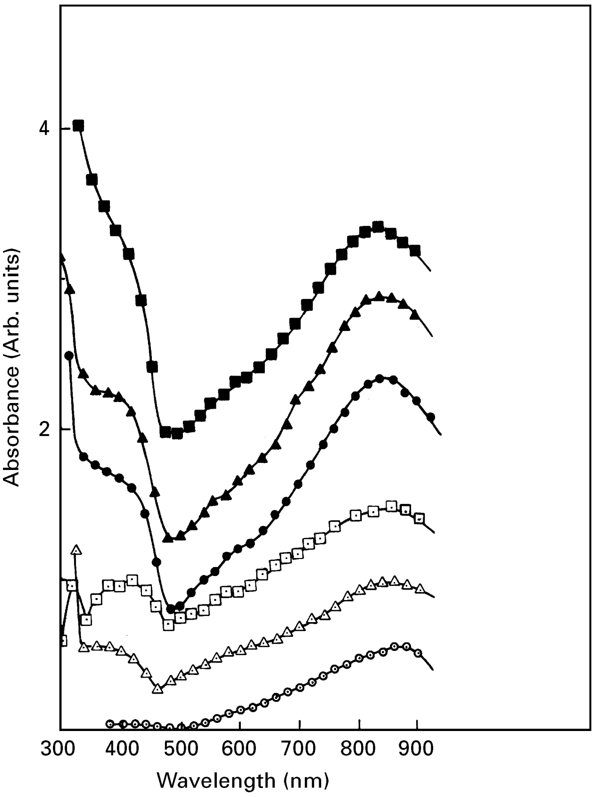

Figure 2 Absorption spectra of poly(*o*-anisidine) film as a function of amount of NaCl added in a solution of pH 2.1: (⊙) No NaCl, (△) 0.2 M, (⊡) 0.4 M, (●) 0.6 M, (▲) 0.8 M, (■) 1.0 M. Deposition time = 5 min.

phase of the polymer. In contrast with this, selective deposition of the insulating fully oxidized pernigraniline (peak ~ 540 nm) is found to take place at the electrode surface by raising the solution pH to 4.13. In the case of the films deposited at an intermediate pH of 2.1, the growing emeraldine salt phase (~ 850 nm) is observed together with a small fraction of fully oxidized pernigraniline fragments (shoulder ~ 540 nm). The observed changes in the peak position values as a function of pH of the solution are attributed to the availability of the number of protons for the polymerization process so as to form conducting as well as insulating phases. Details are reported in our earlier work [6].

From the above results, a pH of − 0.21 appears to be appropriate to yield selective deposition of a conducting phase of polymer. However, it should be noted that in highly acidic solutions, a large amount of carcinogenic benzidine derivatives are known to be produced as a by-product simultaneously with the formation of polymer during electrolysis [7]. Under such circumstances, optimizing the parameters such that exclusive deposition of the conducting phase could be possible by avoiding the formation of an appreciable amount of benzidine derivatives, would be more advisable. For this, the solution pH of 2.1 turns out to be suitable, although the fraction of the conducting phase formed is relatively small compared to that at − 0.21 pH. None the less, at this pH, the addition of an external supporting electrolyte to the solution is essential to make the solution conducting. Therefore, it was thought worthwhile to examine the effect of supporting electrolyte on the extent of formation of the conducting phase. To our surprise, it was observed from the optical spectra (Fig. 2), that apart from the increase in the total absorbance, the selectivity in the formation of the conducting phase increases with the amount of supporting electrolyte in the solution. Also, interestingly, when the absorbance corresponding to the conducting phase ~ 850 nm is plotted versus the concentration of NaCl it shows a linear nature (Fig. 3) with the intercept signifying the amount of conducting phase obtained in the absence of supporting electrolyte in the solution. This clearly demonstrates that the supporting electrolyte plays an important role in deciding the formation of the conducting phase.

These results can be explained by considering the amount of total charge required for the formation of the conducting phase during polymerization. In the absence of a supporting electrolyte in the medium, a major part of the applied current is utilized to compensate or overcome the large ohmic drop, while only a fraction is available for polymer deposition. As a consequence, one observes a lower absorbance as well as a lack of selectivity. Further, by increasing the amount of NaCl in the medium, the resistivity of the medium decreases, leading to the deposition of a greater fraction of polymer, together with an enhancement of the selectivity in the formation of a particular phase. Another possibility which cannot be ruled out is the trapping of Na^+ and Cl^- ions in the deposited films as poly(*o*-anisidine) is known to possess permselective behaviour in an aqueous solution.

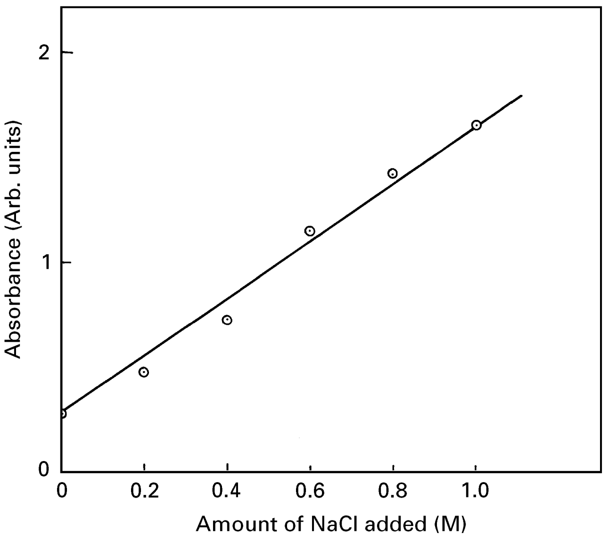

Figure 3 A plot of absorbance versus concentration of NaCl added in an electrolyte solution (absorption wavelength = 850 nm).

The appearance of the Na^+ peak (~ 1075 eV) in the general scan of the XPS spectrum (Fig. 4) gives evidence for the above statement. Detailed studies concerning the surface characterization using XPS are under consideration. The trapped ions may act as charge-compensating species of the polymer, causing restricted mass transfer, and thereby contributing towards improvement in the conductivity of the material. Our results are in agreement with those reported by Chartier *et al.* [8] for polyaniline.

The studies pertaining to the thermal behaviour of the deposited polymer are in agreement with the spectral results. Fig. 5 depicts the thermogravimetric profiles of the polymer films deposited in the presence of electrolyte solutions containing 0.2, 0.6 and 1 M NaCl. As observed from the thermograms, the polymer is seen to decompose in three stages, with the final decomposition temperature extending up to 800 °C [9]. Differences in the thermograms are observed in terms of fraction of the stable fragments incorporated in the film matrix, which increases from 12% to 55% (the final step) with concentration of NaCl. The reverse trend is noticed in the fraction of less stable and volatile fragments (second step, weight loss 40%–68%) and trapped or adsorbed water molecules (first step, weight loss 5%–20%). In addition to this, the clarity between the individual steps appears to be enhanced as a function of NaCl concentration in the electrolyte solution.

At lower NaCl concentration (0.2 M) the polymer deposited consists of randomly formed small molecular weight segments. This paves the way for easy adsorption or trapping of water molecules as a result of its loosely knit structure. A loss of about 20% is observed taking place ~140 °C. Similarly, the continuous loss in weight constituting about 68% of the weight fraction can be attributed to the loss of the volatile component (Cl^- as Cl_2 or HCl) simultaneous to polymer degradation ~590 °C. However, the last step (~ 12% at 800 °C) represents the loss corresponding to the breakdown and decomposition of higher molecular weight fragments of the polymer. As the amount of NaCl in the electrolyte solution is increased, the process of polymer deposition is expected to follow a more ordered pathway. Hence, selectivity in the deposition increases as also do the well-separated three steps. Therefore, the fraction of higher molecular weight fragments is observed to increase, leading to a greater loss in weight in the last step of the TG curve (~45% and 55% at 0.6 and 1 M NaCl concentration). Conversely, the fraction of lower molecular weight fragments is bound to decrease, which

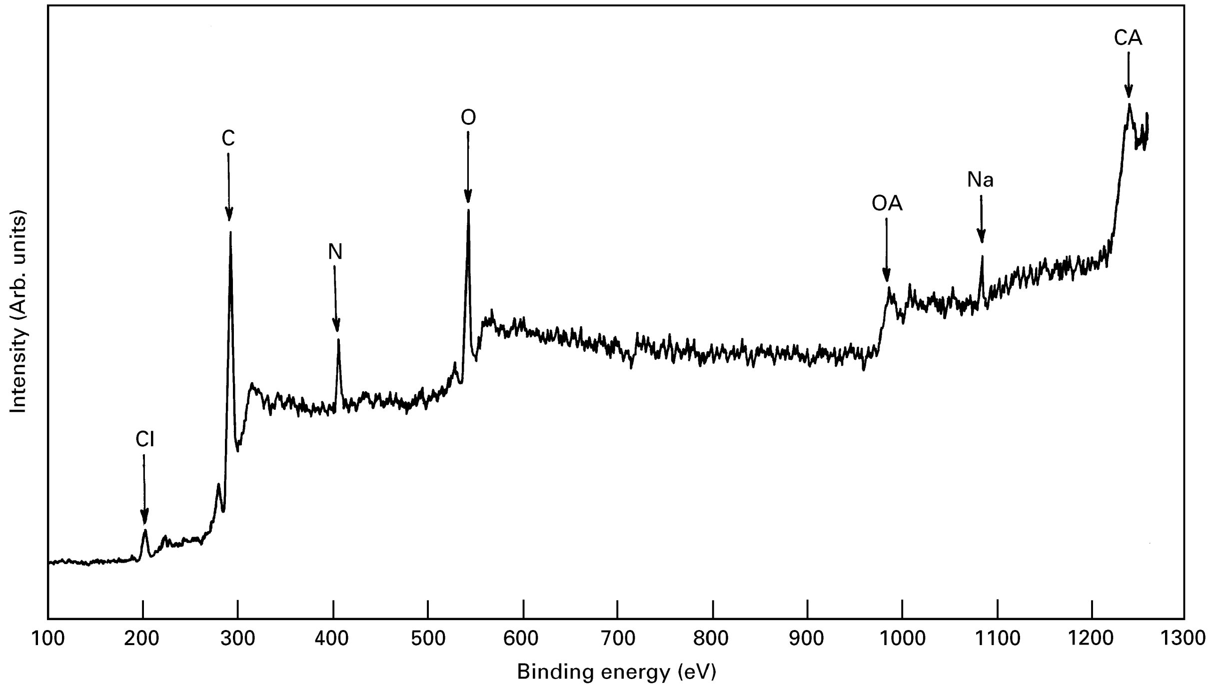

Figure 4 General scan of X-ray photoelectron spectra of poly(*o*-anisidine) film deposited from a solution containing 1 M NaCl as supporting electrolyte. Deposition time = 20 min.

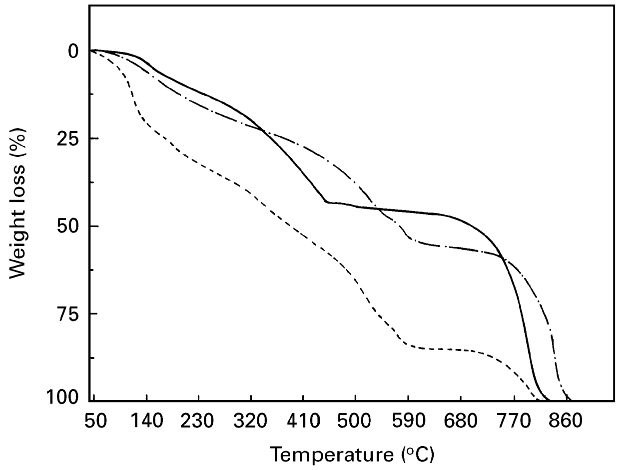

Figure 5 Thermograms of electrochemically deposited poly(-poly) (*o*-anisidine) films as a function of NaCl concentration.NaCl added: (- - - - -) 0.2 M, (—) 0.6 M, (—·—) 1.0 M. Deposition time = 5 min.

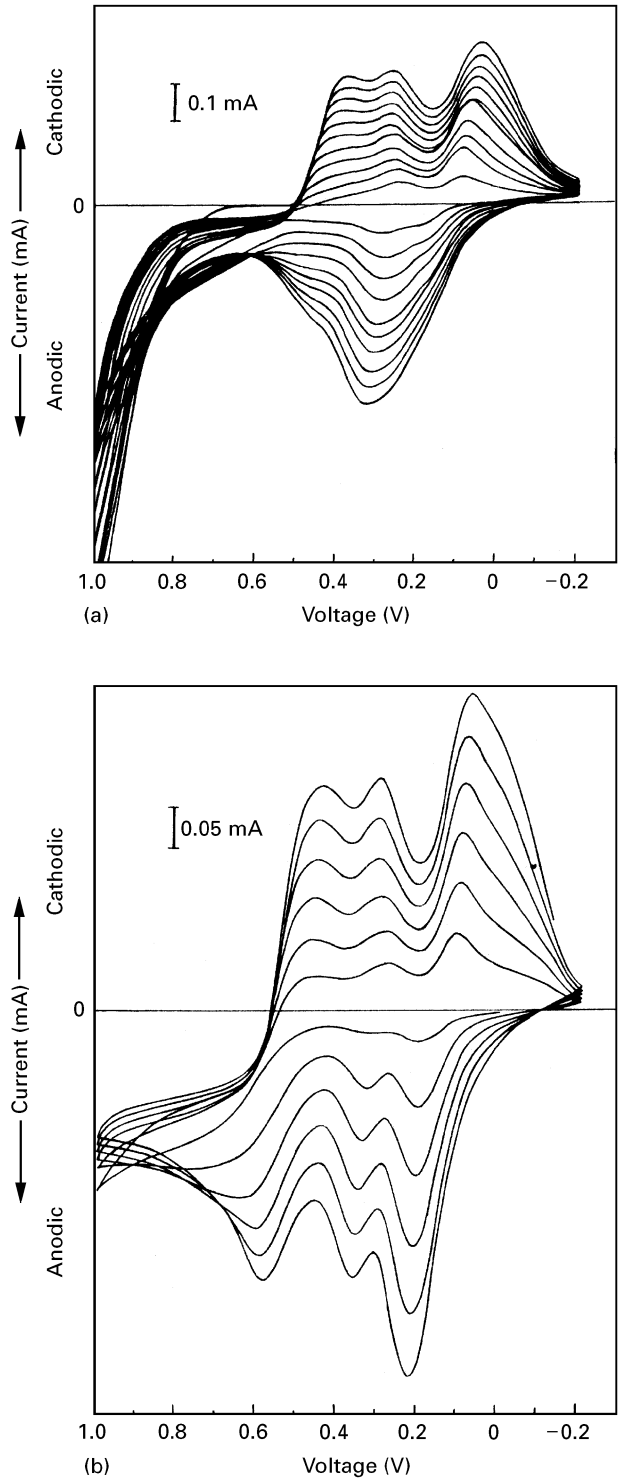

Figure 6 Cyclic voltammogram of electrochemically deposited poly(*o*-anisidine) films (a) without NaCl, (b) with 1 M NaCl.

accounts for lower per cent loss (~45% and 40% in the presence of 0.6 and 1 M NaCl). Similarly, the decrease in the per cent loss (10% and 5% at 0.6 and 1 M NaCl) in the first step is attributed to the smaller fraction of H_2O molecules being trapped in the polymer matrix. The plateau region observed between 450 and 700 °C in all cases, probably arises due to the cross-linking reaction leading to complete decomposition at ~800 °C.

A pair of cyclic voltammograms of the polymer films was obtained by carrying out deposition at a solution pH of 2.1 in the presence and absence of NaCl in the solution, as depicted in Fig. 6. Comparison of the two cyclic voltammograms reveals the presence of three redox couples in each case, and the nature of the peak potential is found to be independent of the cycle number. However, the redox couples are seen to be well distinguished from each other in the film deposited in the presence of the supporting electrolyte as compared to that deposited in the absence of NaCl. Details of the peak potentials of the cyclic voltammograms are given in Table I.

The first redox couple E_{a1}–E_{c1} arises due to the formation of radical cations via oxidation of amine nitrogen, while the second peak E_{a2}–E_{c2} can be attributed to the formation of soluble benzidine derivatives [10]. The benzoquinone produced as a result of hydrolysis represents the third redox couple E_{a3}–E_{c3} [11, 12]. Because it is known that the first cycle voltammetric features generally depend on the nature and orientation of the substrate surface, the absence of the third redox couple in the initial few cycles (up to the third cycle) is attributed to lattice mismatch with respect to the substrate structure. Also, if one considers the growth mechanism, it might be possible that the process of growth does not continue unless radical cations formed in the solution produce seeds on the electrode surface to render further growth, due to which, in the first few cycles, the peak of benzoquinone is not visible. Once the electrode surface is covered completely, further oxidation leads to the formation of diradical dications which may catalyse the polymerization process or react with water to produce benzoquinone. Well distinct peaks are obtained in the cyclic voltammogram of the film deposited in the presence of NaCl (Fig. 6a) as the supporting electrolyte in the deposition medium, because the faradaic current is neither limited by ohmic drop nor by poor mass transfer. As a result, peak current continues to grow as depicted in Fig. 6a. In contrast to this, in the absence of NaCl (Fig. 6b) in the deposition medium, the resistivity of the solution is very high, hence a combined effect of high resistivity of solution as well as

TABLE I Peak potentials of the redox couples observed in cyclic voltammograms during the fourth cycle

	Peak potential (V)					
	E_{a1}	E_{c1}	E_{a2}	E_{c2}	E_{a3}	E_{c3}
1 M NaCl	0.21	0.08	0.32	0.29	0.56	0.43
No NaCl	0.14	0.07	0.28	0.25	0.47	0.40

high resistance of the film contributes towards the ohmic drop, causing poor current efficiency. This diminishes the peak current, as manifested by the absence of well-resolved peaks of the cyclic voltammogram.

4. Conclusion

The solution pH of 2.1 serves as an optimum pH to yield good quality adherent films of poly(*o*-anisidine) constituting a greater fraction of conducting emeraldine salt phase, with the formation of benzidine derivative being suppressed. The supporting electrolyte added to the electrolyte solution is found to play an important role in governing the polymerization process. The properties of the resulting polymeric films deposited as a function of NaCl concentration, are noted to be improved from thermal and redox studies.

Acknowledgements

R. C. P. thanks CSIR for financial assistance. A. G. B. thanks the Third World Academy of Science (TWAS) for providing a research grant.

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Received 27 January
and accepted 13 June 1996