Electrosynthesis and characterisation of polyaniline with and without SDS modification

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Polyaniline films grown under galvanostatic control have been tested in the presence and absence of sodium dodecyl sulphate, with a view to explore the possibility of improvement in their electrochemical characteristics. Cyclic voltammetric studies suggest that the immobilized surfactant enhances electron transfer kinetics because of which the composite structure shows increased conductivity. Chronoamperometric and coulometric behaviour of the electrosynthesised polymer films with and without the surfactant have also been investigated. The results indicate that there is a definite possibility of improvement in the electrochemical characteristics of the electrodeposited polyaniline films upon immobilization of the surfactant.

Electrically conducting polymers are of immense contemporary interest. These substances are endowed with the ability to combine high and variable electrical conductivity with properties of polymeric materials such as high strength, light weight, flexibility and ease of fabrication. Their applications in the development of batteries, sensors, corrosion inhibitors and capacitors are being actively investigated. A salient feature of a conducting polymer is the possibility of its switching from the conducting to the non-conducting form as a result of reduction of the polymer and then making it conducting again by oxidation.

Amongst the various conducting polymers, polyaniline has attracted particular interest over the last decade. It offers extensive chemical versatility, which allows the properties of the polymer to be tuned to meet more appropriately the needs of a given application.

In the present note we describe properties of electrochemically grown polyaniline films in the presence of anionic surfactant, sodium dodecyl sulfate (SDS). Galvanostatic method employed earlier has been used for the growth of the polyaniline films. These studies show that the electrosynthesised polyaniline films need improvement in conductivity. In the presence of surfactant, there are reasons to believe that the electrochemically grown polyaniline films may exhibit enhanced conductivity. Accordingly, electrical and electrochemical behaviour of polyaniline films bearing immobilized SDS have been investigated. These composite structures exhibit substantial improvement in electrical conductivity.

Experimental

All the chemicals used were of AR grade and all solutions were prepared in distilled water. Aniline (BDH) and SDS (CDH) were used as such.

An EG and G Princeton Applied Research 273 potentiostat/galvanostat in combination with a personal computer was used for cyclic voltammetric and chronoamperometric studies. The three-electrode setup used consisted of a platinum working electrode (0.25 cm²), a titanium counter electrode (2.0 cm²) and a saturated calomel electrode (SCE) as the reference electrode. The metal electrodes were carefully cleaned and rinsed in acetone and distilled water.

The polyaniline films were anodically synthesized galvanostatically in 1 M HCl aqueous solution containing approximately 5% aniline by volume. The current density was maintained at 0.1 mA cm⁻² for 15 min to prepare the films. For electrochemical synthesis, a constant current source (LAKE SHORE - 120) was used.

Cyclic voltammetric, chronoamperometric and coulometric studies were carried out using platinum and titanium supported polyaniline films immersed in 1 M HCl with and without SDS. Surface tension was measured using a Tensiomat 21 (Fischer Scientific Instruments, USA).

Results and discussion

Electrochemically formed polyaniline films were subjected to cyclic voltammetric examination at different scan rates in the potential range -0.2 to 1.0 V versus SCE in aniline free 1 M HCl. Cyclic voltammograms were obtained in the absence and presence of 10 mM SDS (CMC = 8 mM) at 10-50 mV/s. The redox reactions responsible for the appearance of peaks I to IV have been extensively investigated and are well understood. The voltammograms show well resolved peaks corresponding to two reversible pro-
### Table 1—Cyclic-voltammetric study of polyaniline film in 1 M HCl

<table>
<thead>
<tr>
<th>Scan rate (mV/s)</th>
<th>( I_p^A ) (mA)</th>
<th>( I_p^C ) (mA)</th>
<th>( E_p^A ) vs. SCE (V)</th>
<th>( E_p^C ) vs. SCE (V)</th>
<th>( \Delta E_p = E_p^A - E_p^C ) vs. SCE (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>I</td>
</tr>
<tr>
<td>10</td>
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<td>-0.78</td>
<td>0.64</td>
<td>0.31</td>
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<tr>
<td>50</td>
<td>-2.66</td>
<td>-1.32</td>
<td>0.96</td>
<td>0.58</td>
<td>0.19</td>
</tr>
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</table>

(a) Without SDS

<table>
<thead>
<tr>
<th>Scan rate (mV/s)</th>
<th>( I_p^A ) (mA)</th>
<th>( I_p^C ) (mA)</th>
<th>( E_p^A ) vs. SCE (V)</th>
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<th>( \Delta E_p = E_p^A - E_p^C ) vs. SCE (V)</th>
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<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>I</td>
</tr>
<tr>
<td>10</td>
<td>-0.83</td>
<td>-0.87</td>
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<td>50</td>
<td>-5.26</td>
<td>-3.42</td>
<td>-3.05</td>
<td>4.42</td>
<td>2.16</td>
</tr>
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</table>

(b) With SDS

### Table 2—Chronoamperometric examination of polyaniline film in 1 M HCl

<table>
<thead>
<tr>
<th>( E ) (V) vs. (SCE)</th>
<th>With SDS</th>
<th>Without SDS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau ) (s)</td>
<td>( I_{max} ) (mA)</td>
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<tr>
<td>1.00</td>
<td>2.20</td>
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<tr>
<td>0.75</td>
<td>3.53</td>
<td>-5.20</td>
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<td>0.50</td>
<td>8.20</td>
<td>-3.08</td>
</tr>
<tr>
<td>0.25</td>
<td>8.50</td>
<td>-1.00</td>
</tr>
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</table>
cesses. The first pair of peaks is due to the oxidation of aniline to radical cation while the second pair of peaks arises due to oxidation of radical cation to radical dication.

It may be noted that the electrochemical activity of polyaniline in the presence and absence of SDS exhibits some distinguishing features: (i) In the presence of SDS appearance of additional peaks V and IV shows enhanced electron transfer kinetics in the presence of immobilized surfactant. Peaks V and VI signify emergence of another redox couple possibly as a result of doping/undoping process. The higher electrochemical reversibility observed with polyaniline films in the presence of SDS suggests that the oxidised form of the polymer undergoes slow irreversible chemical reactions as evidenced by smaller cathodic currents in the absence of SDS. This indicates that the electron transfer is facilitated at the polyaniline film bearing immobilized surfactant. (ii) The peak separations, $\Delta E_p$, (Table 1) are more pronounced in the absence of SDS. This also shows that polyaniline exhibits higher electrochemical reversibility in the presence of SDS. This inference is also supported by larger cathodic reversal currents. (iii) Polyaniline oxidation takes place at less positive potential in the absence of SDS by about 70 mV at scan rate of 50 mV/s. This observation indicates that aniline monomers are more solvated in HCl in the presence of SDS while radical cations, PAN$,^+$, are more solvent in aqueous HCl in the absence of the surfactant. It also shows that the electrogenerated radical cations are quenched by water molecules more quickly in the absence of surfactant.

Other relevant parameters derived from these cyclic voltammograms are summarised in Table 1. Scan rate dependence of cyclic voltammograms of polyaniline films in the presence and absence of SDS, is notable. The peak position is strongly dependent on scan rate. The peaks separate as the scan rate is increased. It is also clear from these results that an electron transfer reaction is more efficient at polyaniline film tested in the presence of the surfactant. Furthermore, in the presence of SDS, the variation of peak current with scan rate is more pronounced and $\log I_p$ varies linearly with $E_{p/0}$. The anodic peak currents when plotted as a function of scan rate with and without SDS show a linear relationship.

Current-voltage studies were carried out for the estimation of electric conductance of the polymer film in the usual manner. Known potential differences in

Fig. 1—Chronoamperometric studies with platinum supported polyaniline film in 1 M HCl at 0.50 V vs. SCE (1. without SDS; 2. with SDS)

Fig. 2—$I \sqrt{t}$ vs time plots for the verification of the validity of Cottrell equation at 0.50 V vs. SCE (1. without SDS; 2. with SDS)
Typical values were found to be $0.76 \times 10^3 \ \Omega^{-1}$ for polyaniline film without SDS and $0.19 \times 10^3 \ \Omega^{-1}$ for polyaniline film with SDS.

Platinum supported electrochemically formed polyaniline films equilibrated with $1M$ HCl were also subjected to chronoamperometric examination at different potentials, both in the presence and absence of SDS (Table 2). Relaxation times at different potentials were estimated from the chronoamperograms. The capacitance values were derived using the relationship:

$$Q = \frac{2FAK}{\sqrt{C}} + M \quad \text{ ... (3)}$$

where $Q$ is the charge in coulombs and $M$ is a constant reflecting double layer charging and adsorption contributions, indicating thereby that the electrochemical process is controlled by transfer of electrons either from or to the conductive coating.

The results presented above indeed show that galvanostatically grown polyaniline films supporting immobilized SDS are endowed with enhanced conductivity. In view of the negative charge borne by the surfactant, the possibility of enhanced electron migration may be ruled out. Since the surfactant is confined to the interface, facilitated electron transfer to the conducting polymer layer seems unlikely. The observed increased conductance may thus be attributed to increased electron transfer kinetics of the electrochemical processes in the presence of the surfactant.

Acknowledgement

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References