Switching response of conducting poly(o-toluidine) in protonic electrolytes

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12 February 1997; revised 12 September 1997

Poly(o-toluidine) film shows multiple optical transitions (yellow → green → blue → violet) depending on the oxidation state of the polymer controlled by varying the potentials in the range from -0.3 V to 1.0 volts versus Ag/AgCl. The presence of methyl group affects not only the polymerization reaction but also the potential window suitable for designing electrochromic devices. A repetitive switching test to estimate the cycle life of the polymer film indicates stable electrochromic behaviour up to $10^5$ cycles, provided the upper potential limit does not exceed 0.55 volts.

Electrochromic devices are based on an electrochemical reaction of a material that displays a visual change upon changing its redox state. Electrochromic devices are characterized by having a memory function, which is one of the basic requirements for a display device, even after the driving voltage has been removed. Electrochromic devices are broadly defined as non-emissive display devices which can exhibit electrically induced reversible colour change. A great variety of physical phenomena such as mechanical, thermal, chemical and electrochemical ones can bring about chromism, although, the main electrochromic devices of practical interest today are based on electrochemical reaction or electro-chemio-chromic (ECC) system. A considerable research effort is currently being devoted to electrochemical studies of conducting polymer films as electrochromic materials. During the last two decades several of the electroactive conducting polymers such as polypyrrole (PPY), polythiophene (PTI) and polyaniline (PANI) have been considered as good candidates for such applications like optical storage devices and optical shutters because of the electrochromic phenomenon.

Among conducting polymers, polyaniline and its substituted analogues have received great attention owing to their good stability in the presence of oxygen and water and also due to their interesting electrochemical properties. In these conducting polymers, colour change, memory effect, various mechanisms of doping and undoping etc have been extensively studied. Polyanilines have electrochemical doping processes different from those in polypyrroles and polythiophenes. Since polyaniline deteriorates upon exposure to more positive potentials, it is necessary to lower down the upper limiting potential limit as much as possible. Recently, it has been shown that the substituted polyanilines (i.e. polyanisidine and copolymers etc.) have greater life time than that of parent polyaniline.

The poly(o-toluidine) (POT) is an important class of polyaniline family. Similar to the parent compound, the optical, chemical and electrical properties of POT depends upon the oxidation states. For example, the fully reduced form of POT (i.e. leucoemeraldine) is colourless although, the fully oxidised form of POT (i.e. perrnigraniline) is violet in colour. These effects are again dependent on the protonation equilibrium, anions and the contact resistance of the polymer. The electrochromism in poly(o-toluidine) has been due to proton and electron exchange along with the simultaneous ingress of anions.

In the present work, an attempt has been made to study the electrochromic effect of poly(o-toluidine) in different protonic acids by varying applied potential. Kinetics of switching reaction, variation with molarity of acid, the colour contrast and life cycles etc have been investigated to help their possible use in electrochromic devices.

Materials and Methods

o-Toluidine and other chemicals of analytical
grade procured from Sigma were used for the electrochromic experiments. Poly(o-toluidine) film was grown potentiodynamically in a cell consisting of three electrodes such as indium - tin - oxide (ITO) coated glass plate as anode, platinum as counter and Ag/AgCl as reference electrode. The potential was swept from -0.2 to 1.0 V in a cell containing 1 M HCl and 0.2 M o-toluidine. The films pertaining to various thicknesses were synthesized varying the time periods. The films were washed with acetone for the removal of oligomers. The photoresponse of POT films were studied in a cell containing two electrodes placed on an optical bench with the illumination of 630 nm of tungsten - halogen lamp (Oriel, USA) through a monochromator (Oriel). The transmitted light were monitored by an Si photodiode (Oriel). The diode output was stored on oscilloscope (Tektronix model 2230) and plotted on a colour plotter (Hewlett Packard). The square wave pulses were applied from function generator (model 501 A) through the electrochemical interface (model 1286). The electrochemical current was being sent to the oscilloscope and recorded in a plotter.

Results and Discussion

The cyclic voltammogram of electrochemically grown poly(o-toluidine) film in 1.0 N HCl medium shows two main redox couples at 0.29 V and 0.56 V vs Ag/AgCl. The first redox peak of POT corresponding to the conversion of amine units in polymer chain to radical cations lies at 0.29 V which can be shown as the interconversion of reduced form to the doped form. This could be subsequently oxidized into imines at 0.56 V as represented by Eq. 1.

The colouration and decolouration in poly(o-toluidine) film proceed with the removal and addition of two electrons and protons on switching the potential between reduced and oxidized states which corresponds to change in different forms of poly(o-toluidine) such as reduced form of POT, leucoemeraldine to polaronic POT form to fully oxidized form of POT, perigraniline.

Figure 1 shows the chronoamperometric response of a ≈ 1.0 μm thin POT film in 1.0 N HCl on cycling the potential between -0.25 to 0.7 V vs Ag/AgCl. The switching response time has been found to be ≈ 27 ms. The magnitude of oxidation and reduction of POT film is found to be approximately of the same order indicating good reversibility. The response time of poly(o-toluidine) is much faster than the polyaniline film which under identical conditions has a switching response of 120 ms. It can be explained on the basis of shift in the torsional angle between the adjacent phenyl rings in poly(o-toluidine) as compared to polyaniline film. It can also be understood on the basis of the change in the dipole moment value which is higher in POT than the parent polymer, which imparts more flexibility to the system.

Figure 2 shows the current response time of ≈ 1.0 μm thick POT film in different protonic electrolytes of same concentration (1.0 M) such as HCl (curve 1), H₂SO₄ (curve 2), HNO₃ (curve 3) and CH₃COOH (curve 4), respectively. During the switching condition of potential from -0.6 to 0.9 V with 1 Hz frequency, the oxidation and reduction take place under the steady state condition. The magnitude of current increase is found maximum for the completely oxidized state. It has been
observed that the magnitudes of current in oxidation and reduction are same except in H$_2$SO$_4$ acid medium. The oxidation current value is high in H$_2$SO$_4$ medium, probably due to the availability of more number of cationic radical sites in sulphuric acid. The basic difference has been found in HCl medium where the response time in POT film is much faster than the other media due to faster proton and electron exchanges and ions insertions. The response time in acetic acid medium is found to be much slower. Acetic acid is weaker ($pK_a \approx 4.76$) than HCl and H$_2$SO$_4$ which have $pK_a$ value $\geq 7$ and as such high voltage is required (-2.0 to 2.2 V) for the complete colour change.

The evaluation of cell performance such as half time periods, switching time etc. have been shown in Fig.3, which shows the optical transmittance vs time for the different protonic acids. In order to determine the switching time the potential is scanned from (-0.4 to 0.9 V) and the corresponding absorption is recorded with the photomultiplier table. It is observed that the variation of colour contrast in different acid depends upon the applied potential and the corresponding curve gives the complete contrast of colour change. The above system pertains that the system is diffusion controlled. The diffusion controlled current is given by

$$i = IA = B^{1/2} n F D_0^{1/2} C_0 f(V-V_o) t^{1/2}$$

where $n$ is the number of electrons participating in the reduction or oxidation, $F$ is the Faraday constant, $A$ is the geometrical area of the electrode, $D_0$ is the diffusion coefficient and $C_0$ is the concentration of the redox species. The function $f(V-V_o)$...
Fig. 4-- Electrochemical current transient in different protonic acid concentration of HCl; curve 1 (0.0001 M), curve 2 (0.001 M), curve 3 (0.1 M) and curve 4 (1.0 M).

Table 1-- The effect of concentration on the electrochromic parameters of POT film in HCl medium

<table>
<thead>
<tr>
<th>Concentration of HCl (M)</th>
<th>Applied voltage (V)</th>
<th>Diffusion coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-0.4 to 1.16</td>
<td>10⁻¹⁰</td>
</tr>
<tr>
<td>0.1</td>
<td>-1.1 to 1.20</td>
<td>1.0 x 10⁻¹¹</td>
</tr>
<tr>
<td>0.01</td>
<td>-1.42 to 1.70</td>
<td>1.2 x 10⁻¹¹</td>
</tr>
<tr>
<td>0.001</td>
<td>-5.0 to 6.82</td>
<td>1.6 x 10⁻¹²</td>
</tr>
</tbody>
</table>

Table 2-- The electrochromic response of ≈ 1.0 μm thick POT film

<table>
<thead>
<tr>
<th>Acid (1.0M)</th>
<th>Applied voltage (V)</th>
<th>Response time (ms)</th>
<th>Diffusion coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>-0.4 to 0.9</td>
<td>116</td>
<td>0.1 x 10⁻¹⁰</td>
</tr>
<tr>
<td>HNO₃</td>
<td>-0.8 to 0.9</td>
<td>125</td>
<td>2.25 x 10⁻¹⁰</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>-0.8 to 0.9</td>
<td>167</td>
<td>1.1 x 10⁻¹⁰</td>
</tr>
<tr>
<td>HClO₄</td>
<td>-0.8 to 0.9</td>
<td>208</td>
<td>1.15 x 10⁻¹⁰</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>-2.2 to 2.0</td>
<td>900</td>
<td>5.0 x 10⁻¹¹</td>
</tr>
</tbody>
</table>

depends on the detailed mechanism of electrochemical reaction and for the ionic diffusion controlled process, f(V-Vₐ) is taken ¹³,¹⁴ to be 1.

Figure 4 shows the current transient of poly(o-toluidine) in different concentrations of HCl; 0.001 M (curve 1), 0.01 M (curve 2), 0.1 M (curve 3) and 1.0 M (curve 4) respectively. It can be observed in POT film that the current response depends upon the number of protons available in the system. In 0.001 M (pH 3) HCl, for the complete colouration and decolouration of POT film the higher voltage has been applied in comparison to 1.0 M HCl where large number of protons are available (Table 1). The current transient with all molarity in HCl has the power fitting. Figure 5 shows the current transient with different protonic acid - curve 1 (HCl), curve 2 (H₂SO₄), curve 3 (HNO₃) and curve 4 (CH₃COOH), respectively. It shows the power fitting and the system can be explained by ionic diffusion process. The value of diffusion coefficient is given in Table 2.

Switching threshold behaviour has also been observed with the application of voltage in 1.0 M HCl. The current flow is diffusion controlled which implies that the threshold behaviour is not only a non-linear function of voltage but also a function of time (pulse width). Thus the electrochromism display based on poly(o-toluidine) tends to be applicable to low formation content display.

Acknowledgement

The authors thank Prof. E.S.R. Gopal, Director, National Physical Laboratory for his keen interest in the present work. D.K also thanks Prof. P.B. Sharma, Principal, Delhi College of Engineering and MHRD, New Delhi for the
financial assistance.

References