

# Electrochromic properties of polycarbazole films

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An attempt has been made to investigate the electrochromic properties of polycarbazole (PCARB) films. Both the electrochemical current response and optical transmittance of an electrochromic cell fabricated using PCARB electrochemically deposited onto an indium-tin-oxide (ITO) glass as an anode and platinum as a cathode have been experimentally measured. Current transients observed for coloration and decoloration of PCARB films have been analysed to delineate the mechanism of switching reaction in these semiconducting PCARB films. © 1997 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Electrochromism is a reversible and visible change in transmittance and/or reflectance resulting from electrochemically induced oxidation/reduction reaction at low voltages. Various organic and inorganic materials such as  $\text{Ir}_2\text{O}_3$ ,  $\text{WO}_3$ , viologens, etc. are known to exhibit electrochromic properties<sup>1,2</sup>. However, recent electrochromic displays based on conducting polymers such as polypyrrole (PPY), polythiophene (PTh) and polyaniline (PANI), etc. have been predicted to show good colour contrast with long cycle lifetime<sup>3–6</sup>. Besides this, conducting polymers have additional advantage in their use for a variety of nonlinear optical applications<sup>7</sup> like optical memory elements<sup>8</sup> and 'smart windows'<sup>9</sup>. It may be remarked that most of these conjugated  $\pi$ -electron rich materials are highly susceptible to chemical or electrochemical oxidation resulting in the modification of their electrical and optical properties.

Polycarbazole (PCARB) and its derivatives have recently been suggested for a number of applications such as redox catalysts, photoactive devices, sensors and electrochromic displays<sup>10–12</sup>. Though Mengoli *et al.*<sup>13</sup> have observed the phenomenon of electrochromism in PCARB, no detailed study has as yet been carried out. PCARB can be electrochemically deposited to yield conductive thin films on desired electrodes and are known to be electrochemically stable and show better redox behaviour in protic acid medium<sup>13–15</sup>. It has been revealed that reduced PCARB films show yellow colour and low conductivity ( $> 10^{-9} \text{ S cm}^{-1}$ ) whereas oxidized PCARB films are green in colour and have enhanced conductivity ( $> 10^{-3} \text{ S cm}^{-1}$ ). The present study was therefore systematically carried out to obtain detailed information on electrochromic properties of PCARB

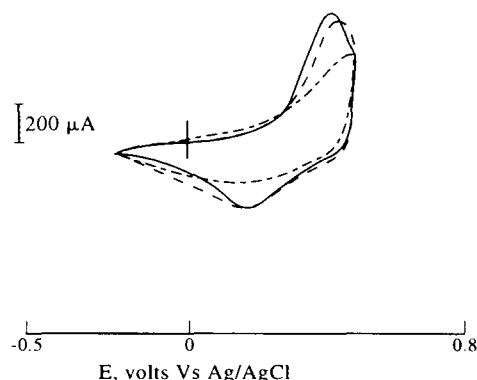
films. In this context, the effect of different acids on the switching time, cycle lifetime and applied voltage on the electrochromic display based on PCARB films have been experimentally measured. Current transients for coloration and decoloration have been analysed to delineate the mechanism of switching reaction in semiconducting PCARB films.

## EXPERIMENTAL

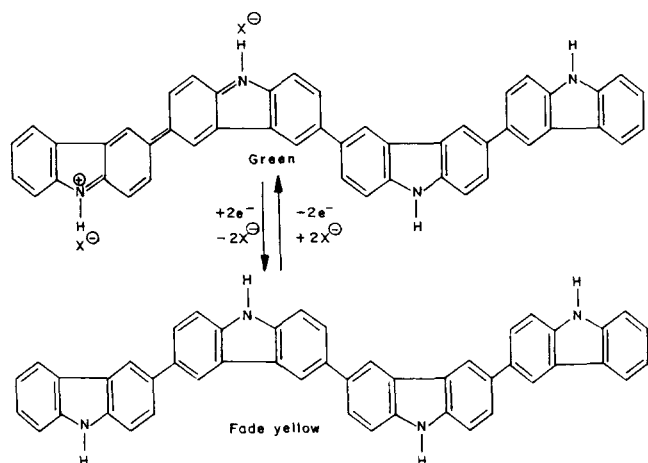
PCARB films have been grown electrochemically in a cell consisting of indium-tin-oxide (ITO) ( $\sim 22 \Omega$ , Balzers, Switzerland) as an anode, platinum as a cathode and silver/silver chloride (Ag/AgCl) as a reference electrode<sup>16,17</sup>. The electrolyte consisted of  $5 \times 10^{-3} \text{ M}$  of carbazole (monomer) recrystallized from methanol, 25% of 5M  $\text{HClO}_4$  acid and 75% of  $\text{CH}_3\text{OH}$  (99%) which are of reagent grade. The PCARB films of varying thickness ( $0.1\text{--}1 \mu\text{m}$ ) were electrochemically obtained by potentiostatic deposition on ITO electrodes at 0.7V for different durations of time. The films were subsequently washed with  $\text{CH}_3\text{OH}$  for removal of any oligomers. The electrochromic studies were carried out in a cell consisting of PCARB/ITO as an anode and a platinum wire as a counter electrode immersed in a solution containing 5M  $\text{HClO}_4$ . The electrical contacts were made with alligator clips after ensuring that there was a minimum contact resistance.

The electrochromic cell was mounted on an optical bench and illuminated with a tungsten halogen lamp (Oriol) through a monochromator (Oriol) at different wavelengths (500–750 nm). The electrochemical current generated as a consequence of application of electrical signal obtained from a Tektronix function generator (FG501A) was measured using a Schlumberger Electrochemical Interface (SI1286). The diode output was

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**Figure 1** Cyclic voltammogram (CV) of a polycarbazole film coated onto ITO electrodes in 1 M HClO<sub>4</sub> (—) 1st scan, (---) after 50 cycles, (· · · ·) after 150 cycles. Scan rate = 20 mV s<sup>-1</sup>



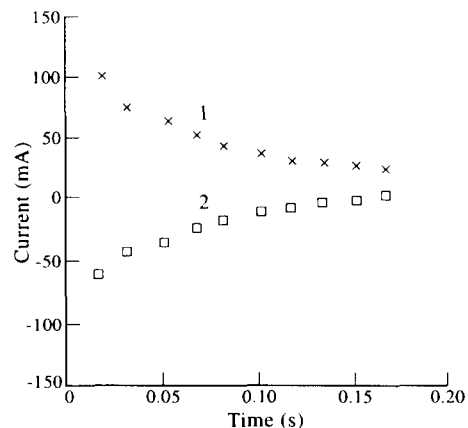
**Scheme 1**

recorded through a Tektronix oscilloscope (model 2230) hooked to an HP colour plotter.

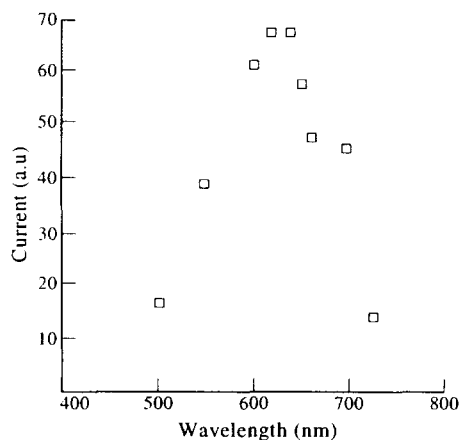
## RESULTS AND DISCUSSION

The cyclic voltammogram (CV) of a PCARB electrochemically deposited onto an ITO electrode recorded in 1 M HClO<sub>4</sub> from -0.2 V to 0.5 V vs Ag/AgCl has been shown in *Figure 1*. In the first scan, two redox peaks can be clearly seen at 0.16 V and 0.44 V, respectively. It has been observed that the colour changes occurred reversibly with the redox potentials resulting in PCARB films becoming transparent fade yellow at -0.2 V and green at 0.5 V. It is significant to note, however, that the colour change worsened with increased cycling (about 150 cycles). Besides this, the colour of the PCARB film faded and changed little with applied potential. It may be mentioned that the shape of the observed cyclic voltammogram (*Figure 1*) was deformed with increased potential cycling. The intensity of the redox peaks gradually decreased with increasing number of scans. Moreover, on increasing the scan limit to higher potential (i.e. up to 0.8 V) leads to faster deterioration of the redox peaks, perhaps causing passivation of the PCARB film.

*Scheme 1* shows the oxidation (green) and reduction (yellow) of PCARB films, X<sup>-</sup> represents Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, and CH<sub>3</sub>COO<sup>-</sup> ions, respectively. The overall redox reaction process involves two electrons and two



**Figure 2** Variation of current (mA) vs time (s) observed for polycarbazole/ 5 M HClO<sub>4</sub> medium, oxidized state: (curve 1), reduced state: (curve 2)

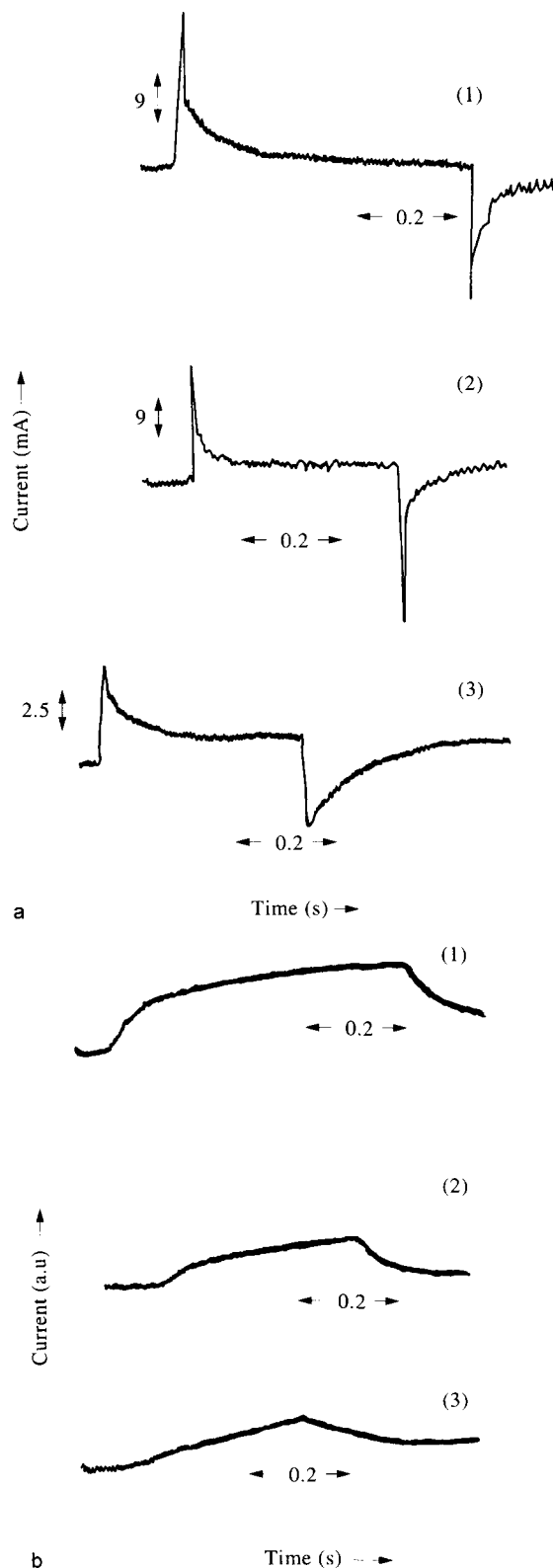


**Figure 3** Variation of optical current vs wavelength (nm) in polycarbazole film

anions resulting in the change of colour in carbazole polymers<sup>15</sup>. From *Scheme 1*, it can be seen that the switching reaction is governed by the inward/outward movement of the counter ions in the film that may in turn be determined by the pH of medium, nature of the electrolyte and the thickness of the film<sup>14</sup>.

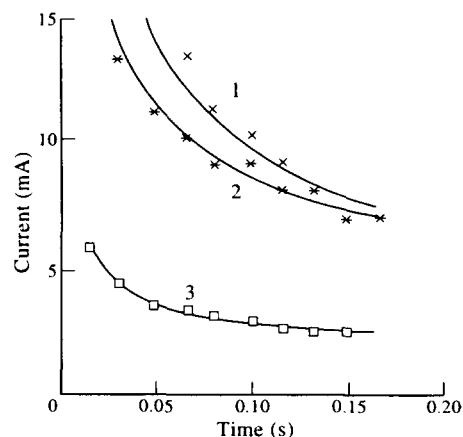
*Figure 2* shows the variation of the observed current with time as a result of the application of voltage. It has been found that the value of the electrochemical current depends strongly upon the nature of substrate on which the PCARB films have been deposited, i.e. the electrochemical current values are higher with Pt surface than ITO. It appears that the oxidation of PCARB film in 5 M HClO<sub>4</sub> medium is perhaps faster than the reduction process. The observed decrease in the value of the current may, perhaps, be due to the variation in the hopping rate of electrons between oxidized (O) and reduced (R) state of PCARB arising as a consequence of counter ion movement.

*Figure 3* exhibits the variation in optical density observed at 1 Hz with potential (-0.6 to 1.0 V) as a function of illumination (500–750 nm). A maximum colour contrast from 640 to 670 nm can clearly be seen. Moreover, it has been observed that there is sufficient colour contrast at 650 nm for recording the change in optical density ( $\delta OD$ ) between oxidized and reduced states.



**Figure 4** (a) Electrochemical current obtained for polycarbazole films with (1) HClO<sub>4</sub>, (2) HCl, (3) CH<sub>3</sub>COOH acids. (b) Optical current obtained as a function of time for polycarbazole films in (1) HClO<sub>4</sub>, (2) HCl, (3) CH<sub>3</sub>COOH media

Figure 4a shows the variation of electrochemical current with time obtained as a function of different acids such as 1 M HClO<sub>4</sub> (curve 1), 1 M HCl (curve 2) and 1 M CH<sub>3</sub>COOH (curve 3), respectively. It is interesting to see that the magnitudes of oxidation and reduction currents are symmetrical for HClO<sub>4</sub> and



**Figure 5** Current transients obtained for polycarbazole films in (1) HClO<sub>4</sub>, (2) HCl, (3) CH<sub>3</sub>COOH media

CH<sub>3</sub>COOH acids but are asymmetrical in the case of HCl. This result may perhaps be attributed to the resistance of electrolyte<sup>18</sup>. Figure 4b shows the variation in the optical absorbance with time obtained in the case of similar cells. These results are in agreement with those obtained by Lacroix *et al.*<sup>19</sup> wherein direct correlation of electrochemical and optical response has been obtained. Table 1 gives the value of half lifetime ( $t_{0.5}$ ) for the observed colour change. The observed switching half lifetime ( $t_{0.5}$ ) from 80 to 208 ms for the PCARB films is similar to the value reported in the case of PPY and PANI, respectively<sup>20</sup>. The slow response time (208 ms) obtained in the case of PCARB/CH<sub>3</sub>COOH film may perhaps be attributed to the weak ionic strength of the acid.

In order to further understand the mechanism of coloration and decoloration the current transients of PCARB films obtained for HClO<sub>4</sub> (curve 1), HCl (curve 2) and CH<sub>3</sub>COOH (curve 3) in Figure 5 have been analysed. The power fit to the curves (Figure 5) clearly shows the diffusion-controlled phenomenon. From these results, it can perhaps be tentatively concluded that the process may either be controlled by the ionic mass transport or ionic diffusion process. The value of the diffusion coefficient has been calculated using the Cottrell equation<sup>20</sup>

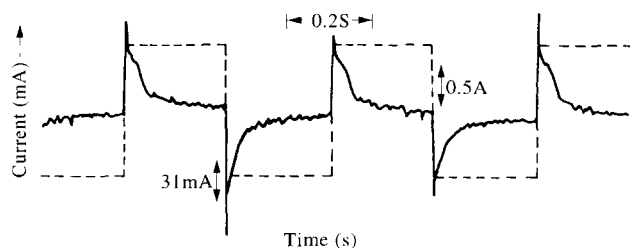
$$i = nFAD_f^{1/2}C/(\pi t)^{1/2} \quad (1)$$

where  $D_f$  is the diffusion coefficient,  $C$  is the concentration of the anions,  $F$  is the Faraday constant,  $A$  is the geometrical area,  $n$  is the number of electrons ( $n = 2$ ) and  $t$  is the half time response. The values of electrochemical switching response time and diffusion coefficient have been given in Table 1. The values of slopes have been obtained from the current transients of Figure 5. The electronic life cycle of the PCARB films varies from  $10^4$  to  $10^5$  and is dependent on the thickness of the film (0.1–0.8  $\mu\text{m}$ ). The thicker films show a lifetime of about  $10^3$  cycles which in turn is dependent on the value of oxidation potential.

Figure 6 shows the variation of current obtained as a function of time resulting from the application of a square wave bias voltage at a frequency of 1 Hz and exhibits the effect of capacitance and resistance of the cell on the observed electrochromic response. The PCARB electrochemical cell can be understood to be a combination of a

**Table 1** Effect of different acids on the electrochromic response of polycarbazole films

Acids	Half lifetime ( $t^{1/2}$ ) (ms)	Applied potential (V)	Slope	$D_f^{1/2}$ ( $\text{cm}^2 \text{s}^{-1}$ ) $\times 10^{-11}$	Process
HClO <sub>4</sub>	108	-0.6 to 1.2	-0.57	0.79	Diffusion
HCl	87	-0.5 to 1.35	-0.43	0.5	Diffusion
CH <sub>3</sub> COOH	208	-0.7 to 3.5	-0.45	3.2	Diffusion
H <sub>2</sub> SO <sub>4</sub>	175	-0.5 to 1.4	-0.52	3.0	Diffusion

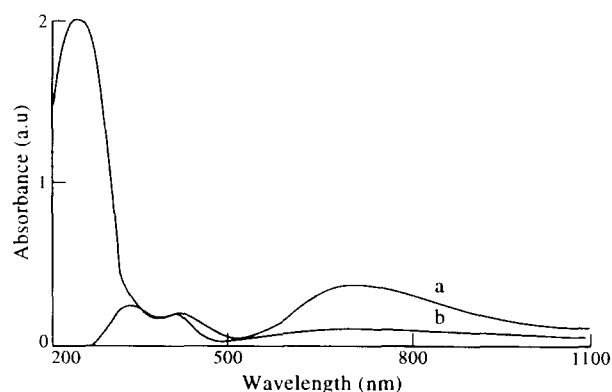
**Figure 6** Current response vs time for polycarbazole film as a result of application of a square wave pulse (1 Hz)

resistor ( $R$ ) and capacitor ( $C$ ) arising due to the realignment of PCARB molecules as a consequence of application of potential. The electrochemical current  $I(t)$  can be described as the sum of the contributions from flow of ions ( $I_i$ ), charge accumulation to capacitor ( $I_c$ ) and charge induced due to the alignment of dipoles in PCARB film ( $I_p$ )<sup>21</sup> and hence can be expressed as

$$I(t) = I_i + I_c + I_p = V/R + C dV/dt + dP/dt \quad (2)$$

where  $P$  is the polarization emanating due to the dipole. The electrochemical current transient does not appear to show the polarization effect, revealing that the change is perhaps associated with the molecular realignment or the dipole orientation resulting in the weak current signal. In the case of a symmetric wave pulse, the PCARB sample switches from the oxidized to reduced state. The magnitude of the observed current transients indicates that there is perhaps a significant effect of resistive and capacitive coupling.

Figure 7 (curve 1) shows the u.v.-visible spectrum of a freshly prepared PCARB film. Absorption bands at 260, 400 and 710 nm, can be seen. The loss of electroactivity of PCARB film after it is cycled for  $10^4$  times is clearly apparent in the u.v.-visible spectra (curve b, Figure 7) as the intensity of the u.v.-visible absorption bands are weaker than that of the freshly prepared PCARB film (curve a, Figure 7). In this context, however, the reduced intensity of the 710 nm peak indicates that perhaps no

**Figure 7** U.v.-vis spectra of polycarbazole film (a) freshly prepared, (b) after it is cycled  $10^4$  times

more anions ( $X^-$ ) diffuse into the PCARB film. It is interesting to see that the intensity of the band at 400 nm is of the same order confirming once again that the prolonged ( $> 10^4$ ) cycling of PCARB films results in the loss of its electroactivity. Table 2 shows the response times and lifetimes reported for some electropolymerized heterocyclic conducting polymers like polypyrrole, polyaniline including polycarbazole<sup>22-24</sup>. It can be seen that electrochromic behaviour of PCARB is comparable with PPY but is not as good as that of PANI or poly(3-methylthiophene). This may perhaps be attributed to the loss of electroactivity of the PCARB film.

## CONCLUSIONS

It has been shown that electrochromic displays based on PCARB can be fabricated. Such an electrochromic display shows excellent contrast between green (oxidized) to pale yellow (reduced) states. The long response time has been explained in terms of ionic diffusion process. The short life cycle of the PCARB based electrochromic displays has been assigned either to the

**Table 2** Response times and lifetimes of some electropolymerized heterocyclic conducting polymers of thickness 100 nm

Heterocyclic Compound	Electrolyte	Electrode	$t$ (ms)	Life time	Refs
Pyrrole	Et <sub>4</sub> NBF <sub>4</sub>	Pt	80	$2 \times 10^4$	22
	Et <sub>4</sub> NClO <sub>4</sub>	Pt	100	$2 \times 10^4$	
Dimethylpyrrole	Et <sub>4</sub> NBF <sub>4</sub>	Pt	250		22
2,2'-Bithiophene	Et <sub>4</sub> NBF <sub>4</sub>	Pt	80	$10^3$	23
3-Methylthiophene	Et <sub>4</sub> NBF <sub>4</sub>	Pt	90	$> 10^4$	23
Aniline	HCl	ITO	80	$10^6$	24
Carbazole	HClO <sub>4</sub>	ITO	108	$10^4$	Present work

loss of electroactivity or to the dissolution of the film into the solution. Studies are currently under way to improve upon the desired reversibility of the PCARB system using various other supporting electrolytes with a view to obtain increased life cycle and faster response time.

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