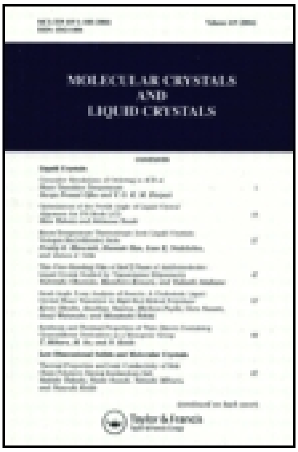

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Structurally Modified Polymer of Carbazole with Specific Catalysis in Electrooxidation of Organic Molecules

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The electrochemical oxidation of carbazole in acetonitrile containing tetra-*n*-butyl ammonium perchlorate produces a green film on the electrode; this film is electrocatalytic to the oxidation of 9,10-diphenylanthracene, or perylene or 9,10-dimethylanthracene or ferrocene. The spectral features of the film reveal a N-N-coupling with a total absence of —NH stretching band. It is soluble in N,N-dimethylformamide. The polymer is structurally modified compared to the film produced by carbazole oxidation in N,N-dimethylformamide.

Keywords: Electrooxidation, carbazole, electropolymerization, catalysis.

The electrochemistry of carbazole in non-aqueous solvents has been investigated with reference to oxidation products,[1,2] the production of excited state[3,4] and conducting polymers.[5–7] Of these investigations the formation of a conducting polymer is of interest in understanding the charge transport mechanisms as this polymer is highly π-conjugated as compared to other known polymers.[8–10] It has been produced by the electrochemical oxidation of carbazole by either potentiostatic or galvanostatic method in N,N-dimethylformamide (DMF) as the solvent. The coupling of the rings in the polymer chain occurs through the 2,2′-positions. The conductivity of this film is comparable to that of polypyrrole.[11] During our investigations on the electrochemistry of carbazole in different non-aqueous solvents such as acetonitrile, methylene chloride, we have generated a green film on the electrode.

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Although this film is lesser conducting than the polypyrrole reported earlier,[11] it exhibits interesting catalysis which is discussed in this paper.

Previous studies[1,2] on carbazole were concerned with the stability of 1*e* oxidation product using tetraethyl ammonium perchlorate as the supporting electrolyte. Carbazole is oxidized at platinum to form a very unstable cation in acetonitrile. This cation radical reacts by deprotonation coupling to the 9,9′- and 3,3′-bicarbazyls. The 9,9′-bicarbazyl is oxidized more anodic than carbazole. The 3,3′-bicarbazyl is more easily oxidized than carbazole itself and produces two reversible one electron waves. Both 9,9′- and 3,3′-bicarbazyls are soluble in acetonitrile. While these features are reproducible, the coupling of the one electron oxidation product is directed to give a N-N- coupling by the use of tetra-*n*-butyl ammonium perchlorate, which results in the insoluble film on the electrode. The role of the supporting electrolytes in the dimerization reactions has previously been investigated[12] with reference to the varying product yields. With carbazole, a mixed coupling of 9,9′- and 3,3′- appears to be occurring through the effect of the supporting electrolyte.

Experimental

Carbazole was obtained from V/O Sojuzcrim Export, Moscow. Acetonitrile was obtained from Fluka Puris Grade (Boiling Point: 80°C). The supporting electrolyte, tetra-*n*-butyl ammonium perchlorate (South Western Analytical Chemicals Co.) was used. 9,10-Dimethyl anthracene (DMA), diphenyl anthracene (DPA), perylene, and ferrocene were procured from Aldrich Chemical Company. Hydroquinone (May & Baker) and N-N-dimethyl formamide (E. Merck, B.P.: 150°C) were used with further purification.

A micro platinum disc electrode (A = 0.017 cm^2) was used as a working electrode. A large mesh platinum gauze electrode was used as a counter electrode and an Ag wire was used as a quasi reference electrode. Cyclic voltammetric measurements were done using a 273 Potentiostat/Galvanostat (Princeton Applied Research Associates) in combination with a 2000 Houston X-Y-t- recorder.

The ir spectrum was recorded using a Jasco (A 200 series) grating spectrometer. Carbazole shows bands at 3550(m), 1620(s), 1480(s), 1350(m), 1280(m), 940(m), 760, 740, 580, 440 cm^{-1}. The spectral features agreed well with the previously reported data.[1,2] The oxidation product in acetonitrile showed the absence of the —NH band;

the oxidation product of carbazole in DMF showed the presence of this band. The polymer formed in acetonitrile further showed a —N—N- band at 1575 cm^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the typical current voltage curve for carbazole in acetonitrile containing 0.1 M $(C_4H_9)_4NClO_4$. The general features of this curve are marked by a broad anodic peak at $E_{pa} = +1.48$ V and a complementary cathodic peak at $E_{pc} = +1.32$ V.[2] With repetitive cycling the anodic peak shifts to a positive value with a corresponding shift of the complementary peak towards a negative value; at the end of 33rd cycle, the anodic peak was situated at $E_{pa} = 1.60$ V and the cathodic peak was located at $E_{pc} = 1.20$ V. The formation of a green film on the electrode was observed upon cycling the potential of the electrode between 0 and +2.0 V. The interesting feature of the

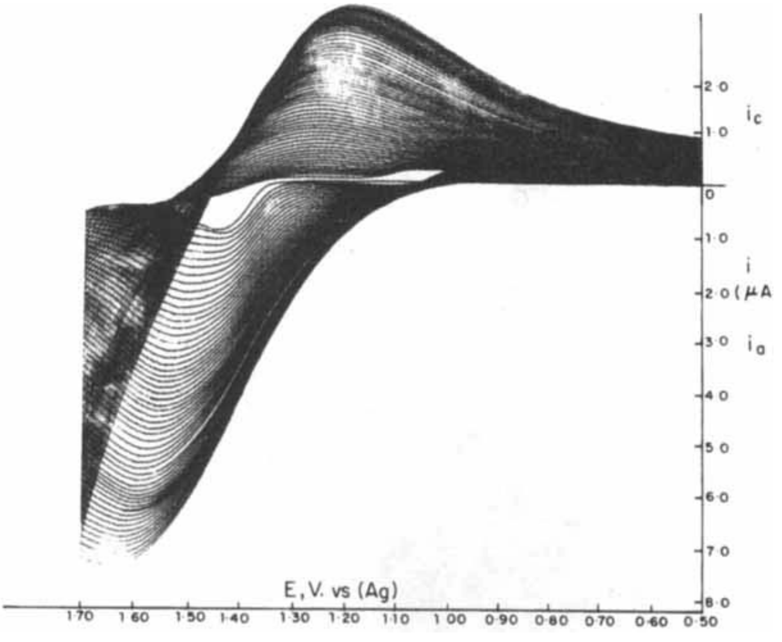

FIGURE 1 Cyclic voltammetric curve for 5 mM carbazole in acetonitrile containing $(C_4H_9)_4N\ ClO_4$. Working electrode: Pt button electrode (A = 0.017 cm^2), Auxiliary electrode: Pt gauze electrode, Reference electrode: Ag wire. Repetitive cycling continuously increases the peak current. Sweep rate: 0.10 V/s.

current-voltage curve shown in Figure 1 is the continuous growth of the peak height upon cycling; generally a diffusion controlled process with a constant area electrode is expected to show a decrease in the peak current due to the growth of the diffusion layer at the electrode.[13] A similar feature of the anodic peak growth was observed in the oxidation of pyrrole in acetonitrile.[14] It appears that the film formation on the naked electrode increases the surface area very effectively for the oxidation of the monomer. The peak current increase is estimated at about 10% per scan suggesting an equivalent increase in the surface area.

During the deposition of the film, an additional cathodic peak is produced at $E_{pc} = 1.05$ V; this is attributed to the product of the oxidation of carbazole as this peak appears only after sweeping the potential of the electrode beyond 2.0 V. The ir spectral features of the film in KBr matrix shows bands (Figure 2) at 1575 cm^{-1} due to N—N stretching. C—N-stretching and the normal —CH stretching in the region 1700–1630 cm^{-1}. The spectrum does not reveal the presence of —NH band which carbazole exhibits at 3400 cm^{-1}. An absorption at 790 cm^{-1} suggests a 1:2:4 trisubstitution indicating the carbazole ring is intact in the polymer. The spectrum also showed the presence of C—C stretching at 1600 cm^{-1}.

The electrochemical characteristics of selected organic molecules have been examined at the filmed electrode. The current-voltage curve of DMA is shown in Figure 3. The two anodic waves of DMA appearing at platinum electrode is also observed at the filmed electrode. The peak currents are higher and the potentials are displaced

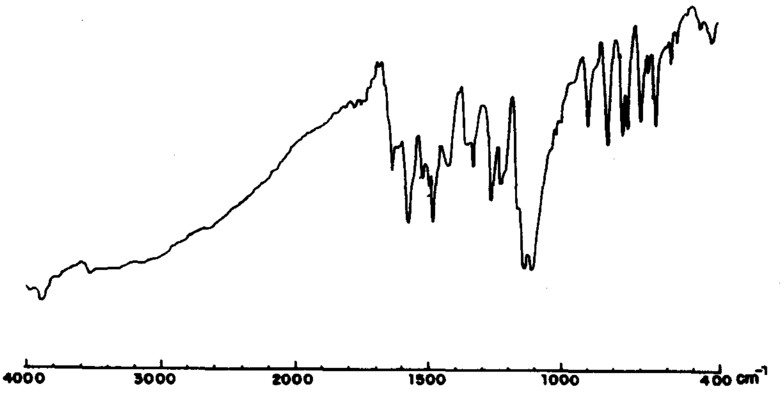

FIGURE 2 IR spectrum of the green film formed by the oxidation of 5 mM carbazole at +2.0 V vs. Ag for about 60 min. The film was pressed along with KBr as pellet for recording the spectrum.

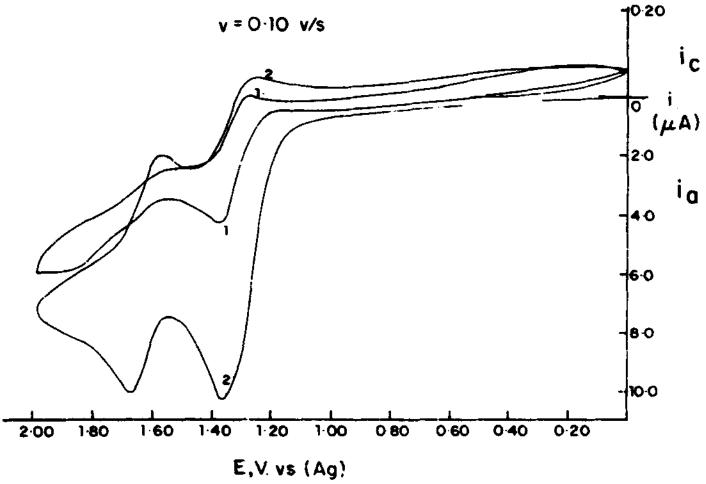

FIGURE 3 Cyclic voltammogram of 2.5 mM 9,10-diphenylanthracene in acetonitrile at platinum (curve 1) and platinum covered with green polymer of carbazole obtained by passing 607 μC (curve 2). Sweep rate: 0.10 V/s for both experiments.

at the filmed electrode; the magnitude of these changes observed in the experiments is shown in Table I. With thicker films on the electrode, the peak currents of DMA are higher. The second peak at E_{pa} = 1.85 V is shifted towards a negative potential at the filmed electrode. For ascertaining the characteristics of the film, a current-voltage curve is recorded in the background solution of acetonitrile containing $(C_4H_9)_4NClO_4$. The film is oxidized at about 0.60 V.

The cyclic voltammetric curve of perylene is shown in Figure 4. The peak current is significantly increased at the filmed electrode

TABLE I

Cyclic voltammetric characteristics of 9,10-dimethylanthracene at the polycarbazole film electrode

Filmed electrode					Pt			
Q μC	E^{I}_{pa} V	i^{I}_{pa} uA	E^{II}_{pa} V	i^{II}_{pa} uA	E^{I}_{pa} V	i^{I}_{pa} uA	E^{II}_{pa} V	i^{II}_{pa} uA
328	1.33	7.0	1.65	5.7	1.37	2.8	1.85	2.3
598	1.33	9.0	1.67	5.2	1.37	2.8	1.85	2.3
1108	1.38		1.67	9.8	1.37	2.8	1.85	2.3
1512	1.38	9.5	1.63	14.5	1.37	2.8	1.85	2.3

Q refers to the total charge passed to film the bare electrode.

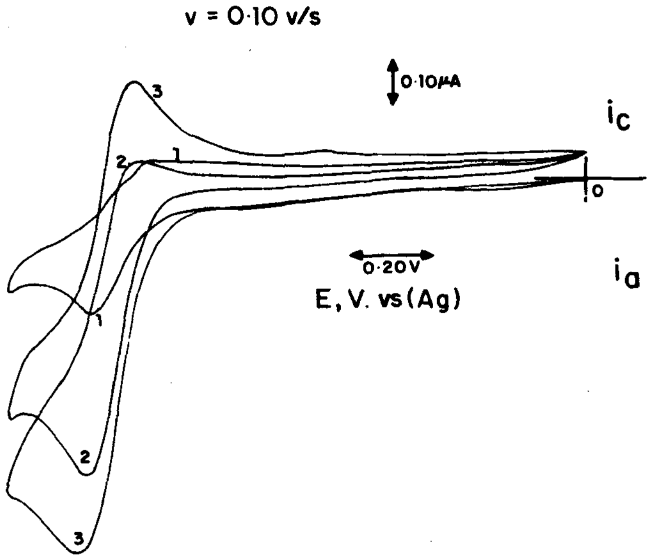

FIGURE 4 Cyclic voltammogram of 5 mM perylene in acetonitrile containing 0.1 M $(C_4H_9)_4N\ ClO_4$ at platinum (curve 1) and platinum covered with green polymer (curves 2 & 3). Sweep rate: 0.10 V/s. The film was formed by passing 910 µC. Curves 2 & 3 represent the steady state and the first cycle recordings.

with a marked stability of the product as revealed by the complementary peak. The magnitude of the peak current increases with the increasing film coverage (see Table II); at thicker films due to the diffusion limiting oxidation of perylene, the peak current increase has shown a declining trend. A similar electrocatalytic behavior was observed with ferrocene.

The electrochemical oxidations of ferrocyanide and H_2Q at the filmed electrode show reduced peak currents; this is attributed to the current being governed by the transport of these molecules through the film with a concurrent transport of the supporting electrolyte ion in and out of the film. The behavior of H_2Q is interestingly different at the polycarbazole film which is formed in DMF. In the latter case, the peak current is nearly two times of the uncovered electrode[15] due to sequestering of H_2Q into the polymer.

Thus electrocatalysis of organic molecules are observed at the new type of carbazole film generated here through

$$P \rightarrow P^+ + e \tag{1}$$

$$P^+ + X \rightarrow X^+ + P \tag{2}$$

TABLE II

Characteristic features of the oxidation of organic molecules at polycarbazole filmed electrode

Filmed Electrode			Pt		
Q μC	E_{pa} V	i_{pa} A	E_{pa} V	i_{pa} A	Δi_p A
I: Perylene					
255	1.30	2.35	1.27	1.12	+1.23
506	1.28	3.05	1.27	1.12	+1.93
804	1.30	10.7	1.27	1.12	+9.58
1008	1.30	4.6	1.27	1.12	+3.48
II: Ferrocene					
600	0.76	5.9	0.75	5.10	+0.80
1000	0.80	8.3	0.75	5.10	+3.20
III: H_2Q					
300	0.45	0.32	0.47	2.35	−2.03
IV: Ferrocyanide					
301	0.22	0.16	0.23	0.63	−0.50

Experiments were carried out using acetonitrile as the solvent. H_2Q is hydroquinone and the experiment was done in 0.1 M K_2SO_4. Sweep rate employed is 0.10 V/S. Δi_p refers to the difference in the peak currents at the two surfaces.

where P is a carbazole film and X is DMA or DPA or Perylene or ferrocene. In addition to the above reactions, the direct oxidation of X might be occurring. The greater stability of X^+ species in the cyclic voltammogram indicates its stabilization in the film matrix. For electrocatalysis to occur at this film, it is necessary for the redox couple to have an $E^\circ > 0.60$ V.

The diffusion of the redox couples through the polymeric film controls the cyclic voltammetric currents. When reactions 1 and 2 are occurring at the electrode, the cyclic voltammetric peak current shows the trend as shown in Figure 5. The peak current increases with increasing film surface excess and shows a decline at higher surface excess values; the declining portion of the curve is attributed to hindrance for the diffusion at thicker films caused by the slower redox processes. A multilayer redox polymer films generally exhibit this behaviour as the redox sites have to react with the diffusing substrate species.[16]

Conclusions

The unusual trend of peak current increase upon repetitive cycling of the electrode potential betwen 0 and +2.0 V in a solution con-

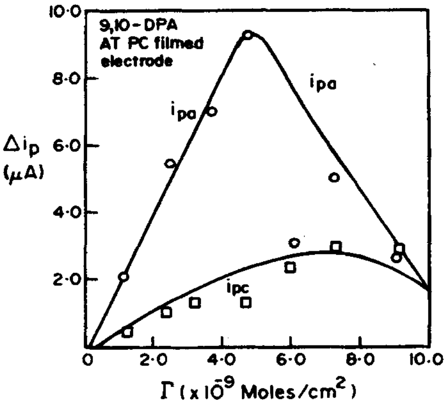

FIGURE 5 Plot of Δi_p vs. surface excess (Γ) for the electrochemical oxidation of 3.6 mM 9,10-DPA in acetonitrile containing $(C_4H_9)_4N\ ClO_4$. i_p refers to the difference in the peak current values at Pt and Pt covered with green film. i_{pa} represents the first anodic peak of DPA and i_{pc} represents the complementary cathodic peak.

taining carbazole and $(C_4H_9)_4NClO_4$ is explained by the increased surface area of the filmed electrode. The catalytic behavior of the new type of carbazole polymeric film is demonstrated by the cyclic voltammetric patterns of DPA, DMA, perylene and ferrocene. The structure of the polymeric film differs from the previously reported polycarbazole which has been generated in N,N— dimethyl formamide as solvent.

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