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Sodium Thiosulphate, a Novel Electrocatalyst in the Electro-synthesis of Electronically Conducting Polymer-Polythiophene.

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Abstract:*In this paper we report on the electrosynthesis of polythiophene from aqueous media with sulphuric acid as the supporting electrolyte. The redox features of polythiophene on a bare carbon graphite working electrode and on a clay montmorillonite host matrix is also reported. Co-polymerisation of polythiophene and polyaniline from an electrolyte media containing both aniline and thiophene monomers reveal that, the redox centres of the two polymers are independent, hence suggesting the formation of a bilayer, even though no charge rectification is observed.The role of sodium thiosulphate as a novel electrocatalyst which has led to a tremendous improvement in the polythiophene faradaic /redox process is also reported*.

Key Words:*Polythiophene, electronically conducting, clay montmorillonite (bentonite), electrocatalyst.*

I. Introduction:

Polyaniline, polythiophene, and polypyrrole are amongst the most well researched of electronically conducting polymers. They have received much in research because of their known unique properties such as low density, well behaved electrochemistry,versatility in methods of production, high anisotropy of electrical conduction, and non-metallic temperature dependence of conductivity .

Electrochemical methods have played a significant role in the characterization and synthesis of these materials. The major advantage of these electrochemical techniques lies in the fact that, they are especially well-suited to the controlled synthesis of these compounds and for the tuning of a well-defined oxidation state.

Despite all the advances made in the study of these novel materials, the preparation, characterization and application of these electronically conducting polymeric systems are still largely un-understood, hence still a major focus of research activity in electrochemistry. The key areas where gaps still exist include understanding the behavior of these systems, in particular on the mechanism of charge transfer and on charge transport processes that occur during redox reactions of conducting polymeric materials. On the applications frontier, research continues on how to perfect their use/application in the fields of energy storage, electrocatalysis, organic electrochemistry, bio-electrochemistry, photo-electrochemistry, electro-analysis, sensors, electrochromic displays, microsystem technologies, electronic devices, microwave screening and corrosion protection etc .

The intensity of research geared towards understanding the electrosynthesis, charge transfer mechanism and possible applications domain for these polymers is captured in the litany of references listed (1-61) and the references therein.

In this paper we report on the electrosynthesis of polythiophene from aqueous media with the mineral acids as supporting electrolyte. This is in contrast to the much used non-aqueous media with large organic salts as supporting electrolyte.

We also report on the novel role of sodium thiosulphate as an electro-catalyst in the polythiophene redox process leading to tremendous improvement in the film electrode transfer kinetics/faradaic process.

II. Experimental Section:

Analytical grade acids were used as received without further purification. The thiophene and aniline monomers were triply distilled until a colorless liquid was obtained prior to use. The liquids were purged using an inert gas and stored under nitrogen.

Triply distilled water or de-ionised water from a Millipore-purification system was used, in preparation of the electrolyte solutions.

The cyclic voltammograms were generated from a potentiostat/galvanostat used in conjunction with a universal programmer which generated the cyclical potential waves. The signals were then fed into an x-y recorder.

The modification of the carbon graphite working electrode was achieved by cycling the potential of the working electrode within a given potential window in an electrolyte solution containing thiophene or aniline monomer. The clay montmorillonite modification of the carbon graphite working electrode surface was achieved as discussed by Orata and Segor (62-63).

III. Results And Discussion:

Electrodeposition Of Polythiophene

On a bare carbon working electrode polythiophene was electrodeposited by cycling the potential from -0.2 V to 0.75 V, 0.80 V, 0.85 V and 0.90 V as positive potential limit. The scan rate was kept constant at 5 mV/sec. The electrolyte solution was 0.1 M thiophene in 1 M H_2SO_4. The resultant cyclic voltammograms are shown in Figures 1 – 4.

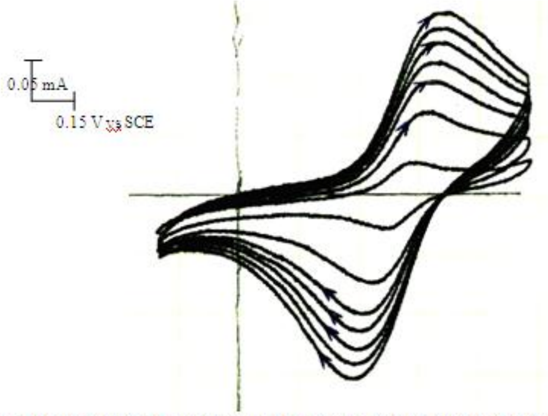


Figure 1. CV response of thiophene electrodeposited on bare carbon electrode in solution containing 0.1 M thiophene and 1 M H_2SO_4. Potential limit -0.2 V to 0.75 V. Scan rate 5 mV/sec.

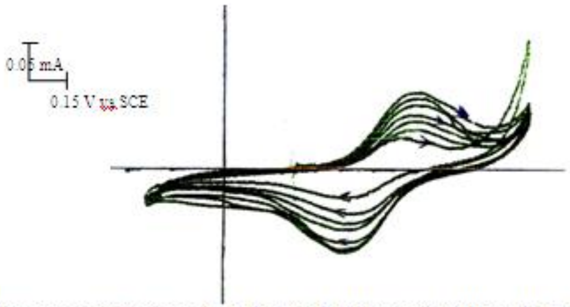


Figure 2. CV response of thiophene electrodeposited on bare carbon electrode in solution containing 0.1 M thiophene and 1 M H_2SO_4. Potential limit -0.2 V to 0.80 V. Scan rate 5 mV/sec.

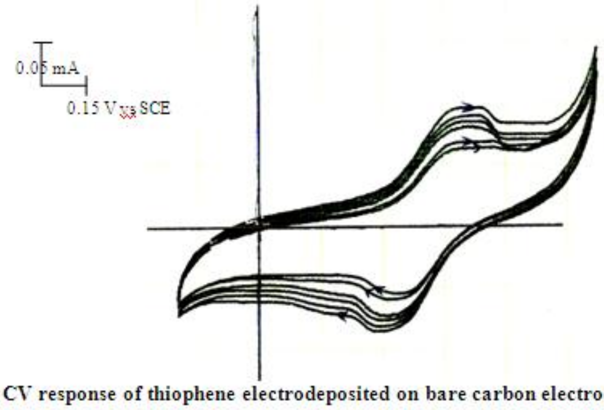


Figure 3. CV response of thiophene electrodeposited on bare carbon electrode in solution containing 0.1 M thiophene and 1 M H_2SO_4. Potential limit -0.2 V to 0.85 V. Scan rate 5 mV/sec.

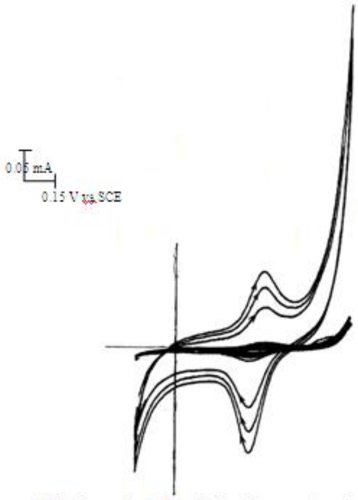


Figure 4. CV response of thiophene electrodeposited on bare carbon electrode in solution containing 0.1 M thiophene and 1 M H_2SO_4. Potential limit -0.2 V to 0.90 V. Scan rate 5 mV/sec.

We observe that, even as the potential limit is increased, the oxidation reduction potential remain unchanged. The rate of electrodeposition of the polymer is quite slow, with very little amounts of polythiophene being electrodeposited.

From the cyclic voltammograms we plotted oxidative peak current ($i_{p,ox}$)versus time for the various potential windows, we observe from the plots (see Figures 1-4) that their rate of change of $i_{p,ox}$ versus time increases with positive potential limit. The oxidative and reductive peak potentials occurred at 0.50 V and 0.35 V respectively.

From the results obtained the CV response becomes more reversible with increasing positive potential limit, i.e., the oxidative and reductive peaks are much more well defined. We propose that as positive potential limit is increased the concentration of thiophene monomer radical cations, necessary for polymerization, increases.

It is important to mention that, the electrolyte solution changed color with time. A UV-visible spectroscopic analysis of the electrolyte solution (at λ_{max}= 612.5 nm) displayed significant changes in absorbance with time (see Figure 5). These observed changes based on Beer-Lamberts law, are a function of the concentration of the chromophores and linked to the extent of conjugation in the system.

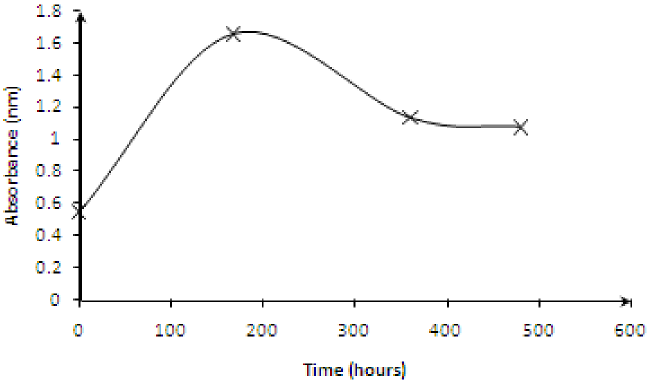


Figure 5. Plot of absorbance (nm) versus time (hours) for electrolyte solution of 0.1 M thiophene in 1 M H_2SO_4.

From the results obtained the CV response becomes more reversible with increasing positive potential limit, i.e., the oxidative and reductive peaks are much more well defined. We propose that as positive potential limit is increased the concentration of thiophene radical cations, necessary for polymerization, increases.

From the cyclic voltammetry features we observe an increase in peak tailing, characteristic of diffusion control processes. A plot of oxidative peak current ($i_{p,ox}$)versus scan rate and square root of scan rate yield a linear plot for square root of scan rate confirming diffusion control for the redox process (see Figures 6).

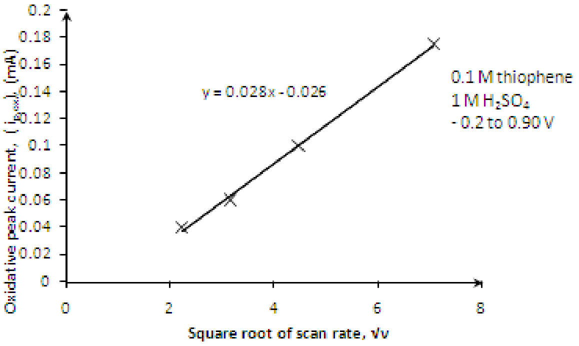


Figure 6. A plot of oxidative peak current (ip, ox) versus square root of scan ratefor electrolyte solution of 0.1 M thiophene in 1 M H_2SO_4.Potential range -0.2 to 0.90 V.

Sodium Thiosulphate As Electrocatalyst in Polythiophene Electrosynthesis:

Even though electrosynthesis of polythiophene in aqueous media yielded much more reproducible voltammograms then hitherto in non-aqueous media, it was important to identify an electrocatalyst which could improve polythiophene redox processes. The chemical substance which formed the ideal candidate for an electrocatalystafter careful evaluation /consideration of its chemistry was sodium thiosulphate.

The next step was then to electrosynthesize polythiophenefrom an electrolyte solution containing 0.1 M thiophene, 2.016 × 10^{-5} moles of $Na_2S_2O_3 \cdot 5H_2O$ (catalyst) in 1 M H_2SO_4. The potential was then cycled from -0.2 to 0.80 V, scan rate 10 mV/sec.

The resultant CV is shown in Figure 7. We observe that the oxidative and reductive peaks are now much more well defined and quasi-reversible.

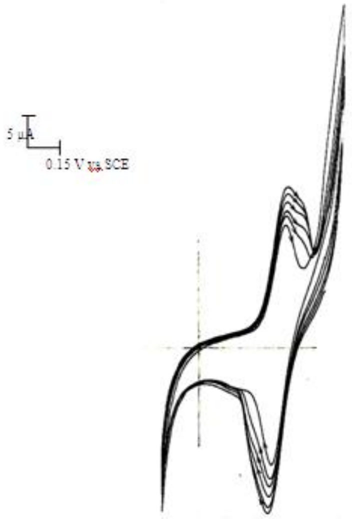


Figure 7. CV response of thiophene electrodeposited on bare carbon electrode in solution containing 0.1 M thiophene, 2.016 × 10^{-5} moles of $Na_2S_2O_3 \cdot 5H_2O$ (catalyst) in 1 M H_2SO_4. Potential limit -0.2 V to 0.80 V. Scan rate 10 mV/sec.

The oxidative and reductive peak potentials occurred at 0.48 V and 0.39 V respectively. We do not observe significant differences in the oxidative and reductive peak potentials. This implies that the catalytic action of sodium thiosulphate does not lead to a decrease in a redox potential which by extension implies that there is no change in the Gibbs free energy (ΔG) associated with the redox system. We therefore propose that the catalytic action of sodium thiosulphate is probably through it affecting the concentration of the radical cations responsible for formation of polythiophene.

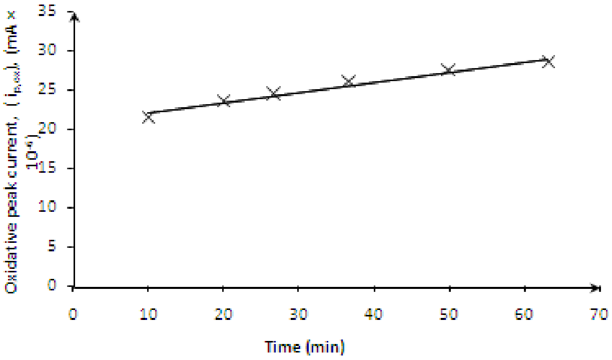


Figure 8. Plot of oxidative peak currents, (ip, ox), (mA) versus time (min) for electrolyte solution of 0.1 M thiophene, $Na_2S_2O_3 \cdot 5H_2O$ (catalyst) in 1 M H_2SO_4, deposited on bare carbon electrode. Potential range – 0.2 to 0.80 V, scan rate 10 mV/s.

The rate of electrodeposition of polythiophene in the presence of catalyst is much higher than in the absence of catalyst. The slope was 0.130 i.e., $\frac{di_{p,ox}}{dt_{(catalyst)}} = 0.130$

It was further observed that when the carbon graphite working electrode potential was cycled from –0.2 to 0.86 Vat scan rate of 20 mV/s in an electrolyte solution containing 0.1 M thiophene and 2.016 × 10^{-5} moles of $Na_2S_2O_3 \cdot 5H_2O$ in 1 M H_2SO_4, completely reversible peaks i.e., ΔEp = 0.00, were obtained (see Figure 9).

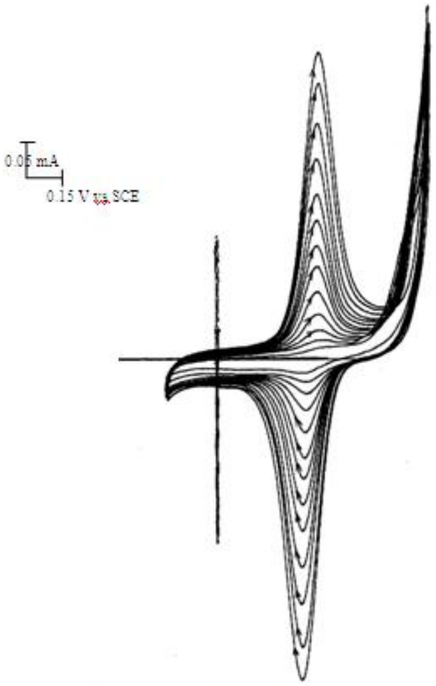


Figure 9. CV response of thiophene electrodeposited on bare carbon electrode in solution containing 0.1 M thiophene, 2.016 × 10^{-5} moles of $Na_2S_2O_3 \cdot 5H_2O$ (catalyst) in 1 M H_2SO_4. Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

At this positive potential limit (0.86V), not only was the oxidative and reductive peaks reversible as is typical of a surface attached species (almost comparable to the behaviour of ferrocene on a platinum electrode) , but also the oxidative potential is now shifted to 0.44 V, representing a shift of 30mV. In this particular case now it appears that the sodium thiosulphatecatalytic action is characterized by a reduction in the oxidative peak potential. This observation on the role of sodium thiosulphate points to its ambivalent catalytic behaviour , which from a thermodynamic standpoint, suggests a reduction in ΔG_{pol}contrary to our earlier observation. The most logical explanation for this observation is tied up in entropic factors associated with the film morphology.

Polythiophene films generated as already described were observed to undergo electrodegradation in the absence of thiophene monomer (see Figure 10). This phenomenon has already been observed in other conducting polymers such as polyaniline.

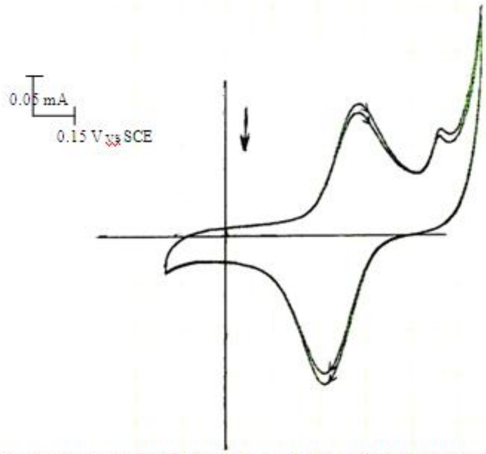


Figure 10. CV response showing electrodegradation of polythiophene film in 0.125 M H_2SO_4 (no thiophene monomer).

We propose that the hydrolysable degradation product formed is a derivative of sulphuroxide/sulphoxide, just as in the case of polyaniline where we form quinone/imine derivative (39,45). When the polythiophene electro-degradation was studied in solution of different pHs i.e., 0.125 M, 0.25 M, 0.5 M and 1.0 M H_2SO_4, in all the cases there was degradation characterized by a decrease in oxidative peak current with each subsequent cycle.

Fresh films of polythiophene were prepared by cycling the potential of the carbon graphite working electrode in a solution containing 0.1 M thiophene and 1 M H_2SO_4. The polythiophene modified electrode was then transferred into solutions containing different concentrations of hydrochloric acid (no thiophene monomer or sodium thiosulphate). We observe once again a reduction in the oxidative peak current (Figure 11).

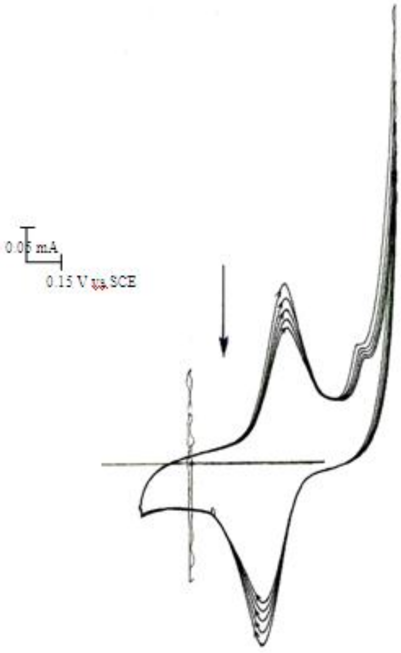


Figure 11. CV response of electrodegradation of polythiophene film in 0.125 MHCl(no thiophene monomer).Polythiophenewas electrodeposited on bare carbon electrode in solution containing 0.1 M thiophene, 2.016 $\times 10^{-5}$ moles of $Na_2S_2O_3 \cdot 5H_2O$ (catalyst) in 1 MH_2SO_4. Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

Once again, we attribute the electrodegradation process to the, formation of hydrolysable sulphoxides. The observation that, the polythiophene film in the HCl does not degrade completely i.e., to zero $i_{p,ox}$.is probably related to the solubility of the degradation products in the electrolyte media. This is probably as a result of intermediate reactions leading to formation of insoluble products during degradation and a reduction in mass transfer. These accumulated products are probably the ones appearing as shoulders, appearing above 0.61 V (see Figure 12).

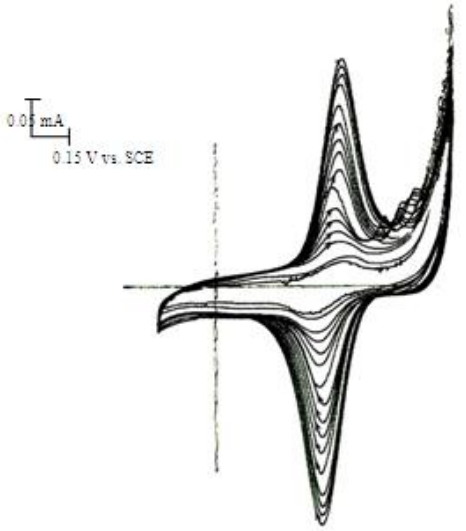


Figure12. CV response of polythiophene in HCl.

Co-polymerisationof PolyanilineandPolythiophene:

Polyaniline and polythiophene was simultaneously electrodeposited by cycling the potential of carbon graphite working electrode from -0.2 V to 0.86 V at a scan rate of 20 mV/sec in a solution containing 0.1 M thiophene, 0.1 M aniline, 1 M H_2SO_4 , and 2.016 × 10^{-5} moles of $Na_2S_2O_3 \cdot 5H_2O$ (catalyst). The resultant cyclic voltammogram is shown in Figure 19.

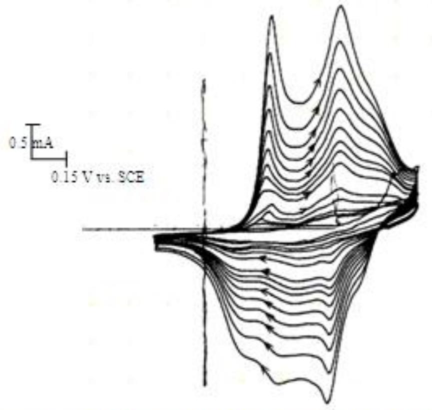
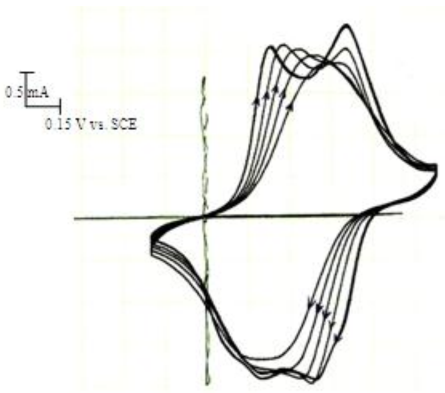


Figure 13. CV response of simultaneous electrodeposition of polyaniline and polythiophene on bare carbon electrode in solution containing 0.1 M thiophene, 0.1 M aniline, 1 M H_2SO_4 and 2.016 × 10^{-5} moles of $Na_2S_2O_3 \cdot 5H_2O$ (catalyst). Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

We observe oxidation peak potentials at 0.27 V and 0.55 V, and corresponding reduction peaks at 0.15 V/0.29 V and 0.49 V. We propose that oxidation/reduction peak at 0.27 V/0.15 V and 0.29 V correspond to the polyaniline redox process. This process is clearly quasi-reversible. We attribute the reduction peak at 0.29 V to be representative of polyaniline reduction peak. The other oxidative peak at 0.55 V and the corresponding reduction peak at 0.49 V represent the polythiophene redox process. It is apparent from the cyclic voltammogram that the polyaniline and polythiophene redox centres are independent. This is a veiled pointer to the formation of a bilayer, even though no charge rectification is observed at the two junctions..

When the polyaniline and polythiophene bilayer was transferred into a solution containing 0.125 M $H_2SO_4$and the potential cycled from -0.2 V to 0.86 V, we observed a reduction in oxidative and reductive peak potentials of both polyaniline and polythiophene. We note that the electrodegradation was much more pronounced in polyaniline as compared to polythiophene (see Figure 14), and it is also observed that the polyaniline oxidative peak potential shifts positively.



igure 14. CV response of electrodegradation of the polyaniline and polythiophene bilayer in 0.125 M H_2SO_4. Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

On the contrary, the oxidative peak potential for the proposed polythiophene peak does not vary. The reductive peaks for both polyaniline and polythiophene shift toward negative potential during the degradation. We propose that being a bilayer the layeral configuration can affect the degradation i.e.,the diffusion of the inner polymer degradation products will be curtailed significantly by the outer polymer. The role of the electrocatalyst in the electrodegradation can only be speculative.

When the polyaniline/polythiophene bilayer was electrodegraded in solution containing 0.25 MH_2SO_4,0.5 M , H_2SO_4, and 1MH_2SO_4,we now observe that the polyaniline and polythiophene oxidation/reduction peaks merge forming oxidation/reduction peaks at 0.46 V, and a broad reduction shoulder spanning 0.18 V-0.32 V. It appears that under these conditions there is a transition from a bilayer to a composite conformation. We also observe that the oxidation peak potential shifts positively with decreasing pH. Similar shifts in oxidation potential with pH have been observed in polyaniline. This observed redox behavior is probably due to the products of polyanilinedegradation(quinone/imine)'trapped' in the matrix, hence the dominant polyaniline redox character.

Simultaneous electrodeposition of polyaniline and polythiophene on a bare carbon graphite working electrode was conducted by cycling the potential from -0.2 V to 0.86 V at a scan rate of 20 mV/sec in a solution containing 0.1 M thiophene, 0.1 M aniline, 1 M H_2SO_4 , and 2.016 × 10^{-5} moles of $Na_2S_2O_3 \cdot 5H_2O$ (catalyst). The resultant cyclic voltammogram is shown in Figure 15.

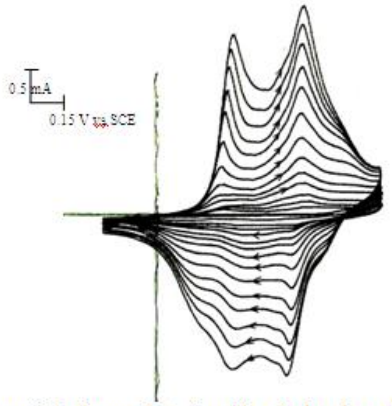


Figure 15. CV response of simultaneous electrodeposition of polyaniline and polythiophene on bare carbon electrode in solution containing 0.1 M thiophene, 0.1 M aniline, 1 M H_2SO_4 and 2.016 × 10^{-5} moles of $Na_2S_2O_3 \cdot 5H_2O$ (catalyst). Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

The film was then transferred to a solution containing HCl (no monomer). We observe the same electrochemical features in HCl as was in H_2SO_4, i.e.,a bilayer with polyaniline and polythiophene redox centres being independent. There is no significant shift in the oxidation and reduction potentials. Even though in the case of electrodegradation in HCl solution (no aniline or thiophene monomer) we observe that thepolyanilineredox peak is relatively unchangedas compared to the polythiopheneredox peak which reduces significantly.See Figure 16.

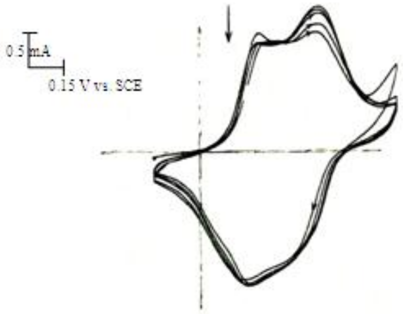


Figure 16. CV response of electrodegradation of the polyaniline and polythiophene bilayer in 0.125 M HCl. Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

The electrodegradation profile is reversed as the pH is decreased, i.e., 0.25 M HCl (see Figure 17).

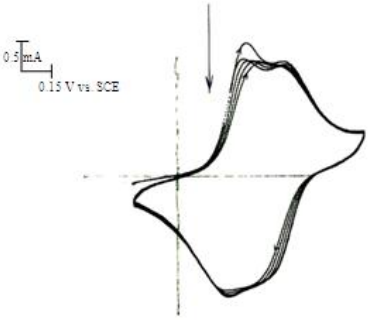


Figure 17. CV response of electrodegradation of the polyaniline and polythiophene bilayer in 0.25 M HCl. Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

We attribute these changes to the presence of chloride anion which is known to have very high charge density. Similarly HCl being a monoprotic acid has a lower proton (H+) concentration as compared to H_2SO_4a dibasic acid, of the same concentration. The proton population in the polymer matrix probably affects the redox process.

Polyaniline and polythiophene were simultaneously electrodeposited from a solution containing 0.1 M thiophene and 0.025 M aniline in the presence of 2.016×10^{-5} moles of sodium thiosulphate catalyst $(Na_2S_2O_3 \cdot 5H_2O)$ in 1 M H_2SO_4. The potential of the bare carbon working electrode was cycled from -0.2 to 0.80 V at a scan rate 20 mV/sec. The resultant cyclic voltammogram had ox/red peaks at 0.18 V, 0.46 V, 0.77 V/0.03 V, 0.43 V, 0.51 V (shoulder). This appeared to be normal peaks, whose characteristics are predominantly polyaniline/quinone-imine peaks. There is no visible evidence of polythiophene peak. When this electrode was transferred to solution containing 0.125 M, 0.25 M, 0.5 M and 1.0 M $H_2SO_4$and the potential cycled from -0.2 V to 0.86 V at a scan rate 20 mV/sec, we observe electrodegradation of features of polyaniline. This is characterized by a decrease in oxidation peak current (see Figure 18).

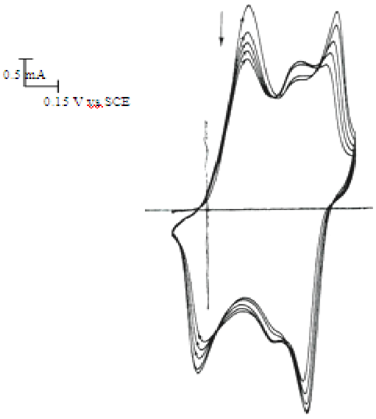


Figure 18. CV response of electrodegradation of the polyaniline and polythiophene bilayer in 0.125 M H_2SO_4. Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

It is worthmentioning, that even as the electrolyte solution pH was decreased, there was an increase in the oxidation potential as the film degraded (Figure 19).

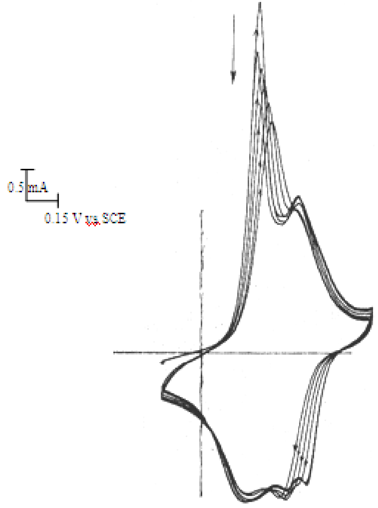


Figure 19. CV response of electrodegradation of the polyaniline and polythiophene bilayer in 1.0 M H_2SO_4. Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

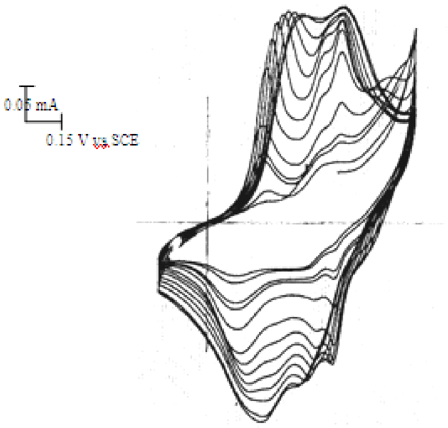


Figure 20. CV response of simultaneous electrodeposition of polyaniline and polythiophene on bare carbon electrode in solution containing 0.1 M thiophene, 0.025 M aniline, 1 M H_2SO_4 and 2.016 × 10^{-5} moles of $Na_2S_2O_3 \cdot 5H_2O$ (catalyst). Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

This shift towards positive potential becomes more pronounced as the pH is lowered. This is probably as a result it having more of polythiophene redox character,since such shifts are not observed in the case of pure polyaniline. We also observe that the presence of polythiophene makes electrodegradation of polyaniline more difficult, in other words it stabilizes the polyaniline film from electrodegradation. This, we speculate, is the result of interference i.e., chemical/electrochemical between the thiophene redox centres and quinone/imine redox centres. This is corroborated by the absence of the characteristic quinone/imine peaks. It is also noteworthy that the film obtained from simultaneous electrodeposition of polyaniline and polythiophene displayed visible photochromic properties characterized by an orange color in the centre of electrode followed by violet/blue and green formations. This is definitely a blend of colors displayed from electrochromic features of polyaniline and polythiophene.

Fresh films were prepared from electrolyte solution containing 0.1 M thiophene, 0.025 M aniline in 1 M HCl as the supporting electrolyte in the presence of 2.016 × 10^{-5} moles of sodium thiosulphate catalyst. The resultant CV have poor electrochemical features. Attempts to degrade the film in 0.125 M, 0.25 M, 0.5 M and 1.0 M H_2SO_4 yielded broad and misshapened peaks with no useful electrochemical information. We propose that these poor electrochemical features can be attributed to the chloride Cl^- anion and high pH of electrolyte solution given that HCl is monobasic acid. The mode of interaction between the Cl^- anion and polyaniline/polythiophene can only be speculative, even though it is known that Cl^-anion has a high charge density, therefore its ingress into either of the films is definitely a lot easier based on steric considerations as compared to HSO_4^-, and SO_4^{2-} ions.

When fresh films of polyaniline and polythiophene were electrodeposited from a solution 0.1 M thiophene, 0.025 M aniline, [thiophene] > [aniline], in 1 M H_2SO_4in the presence of 2.016 × 10^{-5} moles of sodium thiosulphate catalyst and the potential cycled from -0.2 V to 0.86 V at a scan rate 20 mV/sec, the resultant CV is shown in Figure 21.

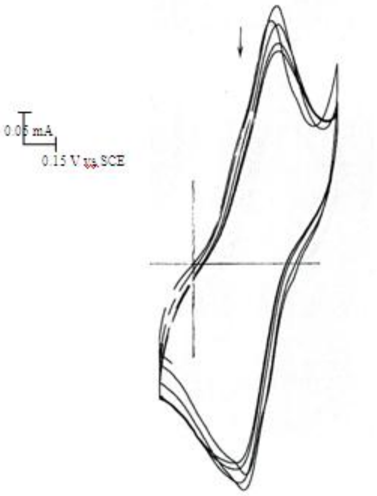


Figure 21. CV response of electrodegradation of the polyaniline and polythiophene bilayer in 0.125 M HCl. Potential limit -0.2 V to 0.86 V. Scan rate 20 mV/sec.

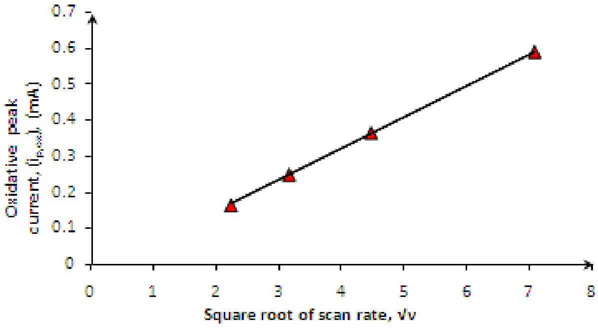


Figure 22. A plot of oxidative peak current (ip, ox) versus scan rateobtained 0.1 M HCl.The potential was cycled from-0.2 to 0.86 V at a scan rate of 20 mV/sec.

We observe that at the onset of redox process we have distinct peaks whose oxidation potential shifts positively. These peaks other than for the increasing oxidation potential, are characteristic of polyaniline. The second set of oxidation peaks are observed at 0.49 V and 0.58 V. The latter are reminiscent of quinone/imine peaks. The reduction peaks form a broad band at 0.31 V-0.44 V. We observe that the two oxidation centres merge on continued potential cycling. We propose that the transition from independent redox centres to merged/composite redox centres represents a transition from a bilayer to a composite formation.

When the film was transferred to electrolyte solution containing 0.125 M, 0.25 M, 0.5 M and 1.0 M HCl,we obtain a single redox peak. On continued cycling of the potential we observe a decrease in the oxidation peak current and an increase in the oxidation potential with each subsequent cycle (see Figure 22). The observation that the first peak is lower than the second peak is probably as a result of solvent population in matrix. Such a phenomenon has been observed in the case of polyaniline (39) where the oxidative peak current for the first scan is always higher than that for subsequent scans.

When scan rate dependence studies were conducted, a plot of the oxidative peak current versus square root of scan rate yielded a linear curve.. This suggests that the process is diffusion limited (see Figure 23).

II. Conclusion:

The results presented in this paper highlight the electrodeposition of polythiophene in an aqueous electrolyte media with sulphuric acid as the supporting electrolyte.

The redox properties and features of the polythiophene film obtained were much more well defined then those reported for polythiophene, electrodeposited in non-aqueous media with large organic salts as supporting electrolyte.

It has also been shown that, sodium thiosulphate, plays the role of an electrocatalyst in polythiophene electrosynthesis/ redox process. From the cyclic voltammetric profile, we observe tremendous improvement in the electrode transfer kinetics/faradaic processes as demonstrated by complete reversibility of the redox peaks. It is thus instructive that, more research be conducted geared towards identifying other new and more efficient electrocatalysts not only for polythiophene redox process, but also for other conducting polymers, as these electrocatalysts might be the missing link required in improving the processability of these polymers, hence opening them up for new applications.

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