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Electrochemical Studies of Reactive Blue - 4 on Glassy Carbon Electrode with Polyaniline

C. Sathish Prabu^{a*}, B. Sowjanya^b, R. Manikandan^c, K. Swaminathan^d

^aAssistant Professor, Department of Chemistry, Kuppam Engineering College,
Kuppam, Chittoor Dt, Andra Pradesh, India

^bAssistant Professor, Department of Chemistry, Kuppam Engineering College,
Kuppam, Chittoor Dt, Andra Pradesh, India

^cAssociate Professor, Department of Chemistry, PRIST Deemed to be University,
Thanjavur, Tamilnadu, India

^dAssociate Professor, Department of Science & Humanities, P.R Engineering College,
Vallam, Thanjavur, Tamilnadu, India

*Corresponding Author: C. Sathish Prabu, E-mail: cprabusathish@gmail.com

Abstract

The developments in the field of electrically conducting polymers have grown very rapidly since the discovery and there is a very sharp increase in conductivity when intrinsically insulating organic conjugated polymers are doped with oxidizing and reducing agents. An overview of technological developments involving conducting polymers clearly indicates that the field expands at unprecedented rates. The manuscript first introduces the conducting polymers (CPs), conducting mechanism, and concepts of doping and briefly introduces main applications. Different types of CPs, their unique properties and synthesis is discussed. The present review will help the effective implementation of conducting polymers in different fields, which directly depends on the degree of understanding of their behavior and properties. Here the cyclic voltammetric studies of reactive blue 4 (RB 4) was carried out in aqueous solution on glassy carbon electrode (GCE) along with poly aniline. The effect of pH on the electrochemical behavior of reactive blue 4 (RB 4) was performed from pH 1.0 to 13.0 at scan rate 50 mV/s. A systematic study of the experimental parameters that affect the voltammetric response was carried out. Maximum peak current conditions were arrived. Calibration curve was made under the maximum peak current conditions at different concentration RB 4. The concentration range studied for the determination of 200 to 700 ppb. The lower limit of detection is 200 ppb for GCE. The suitability of this method for the quantization of dye in textile industries effluents was also ascertained.

Keywords: Cyclic voltammetry, Reactive Blue 4, poly aniline, Glassy Carbon Electrode

1. Introduction

The developments in the field of electrically conducting polymers have grown very rapidly since the discovery and there is a very sharp increase in conductivity when intrinsically insulating organic conjugated polymers are doped with oxidizing and reducing agents. An overview of technological developments involving conducting polymers clearly indicates that the field expands at unprecedented rates. The manuscript first introduces the conducting polymers (CPs), conducting mechanism, and concepts of doping and briefly introduces main applications. Different types of CPs, their unique properties and synthesis is discussed. The present review will help the effective implementation of conducting polymers in different fields, which directly depends on the degree of understanding of their behavior and properties

1.1. History of conducting polymers

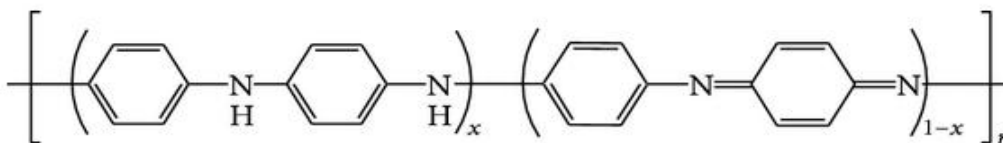
Approximately three decades ago, intrinsically conducting polymers were discovered and this discovery withdraws attention of researchers because of countless applications of these polymers in scientific field. These are also called as synthetic metals as their electrical conductivity is very high analogous to those of metals. [1] The examples of various conducting polymers (CPs) are: polyacetylene, poly furan, polypyrrole, polythiophene, etc. The insulating behavior of polymers can be converted into conducting by carrying out doping of different salts by chemical and electrochemical redox reactions. [2] The highly conducting polysulfur nitride $[SN]_x$ was discovered by Walatka et al. in 1973 . MacDiarmid, Shirakawa and Heeger enhanced the semiconducting behavior of organic polyacetylene in late 1970 which was synthesized by chemical polymerization method. Their work on doping of polyacetylene with halogen derivatives was noticed and published in chemical communication journal in 1977.[3] These three scientists were conferred Nobel Prize in Chemistry in 2000 for the discovery of conducting polymers (CPs). After the discovery

of conducting polyacetylene scientists turned interest in making of other conducting polymers like polythiophene, polyaniline, polypyrrole, polyfuran. In contrary to those of metals, these polymers can be processed at low temperatures but the main problem with these polymers is of their stability.[4-5] The various applications of conducting polymers can be increased by doping with other functional materials to form polymer composites. These are used in different fields like physics, chemistry, electronics, and biomedical science. [6-7]

The hybrid and nanohybrid conducting polymers are synthesized by adding metal, metal oxides, graphene, graphene oxide in conducting polymers. These new materials improve functionality in different areas like in sensors,[8-9] The doped conducting polymers have more capability for corrosion protection than undoped polymers because they give suitable environment for corrosion protection on metal surfaces by restricting movements of corrosive agents or forming a uniform passive layer of doped polymers on metal surfaces [10-12].

1.2 Polyaniline

Polyaniline (PANI) represents one of the most important conducting polymers and received lot of attention due to its controllable electrical conductivity, environmental stability, and interesting redox properties associated with the chain hetroatoms. The PANI family of polymers has been recognized as an interesting and unusual members of the class of π -electron containing conducting polymers. Unlike many others members of this class viz; polyacetylene, polypyrrole, and polythiophene whose electronic properties are well understood solely on the basis of their conjugated carbon backbones, in PANI a nitrogen hetroatom is incorporated between constituent phenyl (C_6H_6) rings in the backbone.[13] PANI exists in a variety of forms which differ in their oxidation level.



2. Methods and Materials

2.1 List of materials

1. Hydrochloric acid (HCl).
2. Sulfuric acid (H₂SO₄).
3. Ammonium persulfate (APS).
4. Electrochemical cell (15 ml capacity) made of glass.
5. Glassy Carbon Electrode
6. Ag/AgCl was used as reference electrode.
7. 0.1M KCl aqueous solution.
8. DI water

2.2 Methods

Chemical polymerization

In this polymerization monomers can be polymerized by Polyaniline and Polypyrrole were synthesized on various substrates such as Pt, Au, Fe, Al, stainless steel, carbon fibers, brass and zinc.[14-15]. Polyaniline doped with tungstate was also chemically synthesized and characterized by various techniques. The composites films of polypyrrole and polyvinylidene fluoride composite films were formed by chemical oxidation method and ammonium per sulphate used as oxidant. The nanocomposites of polypyrrole with copper sulfide were synthesized and characterized by various techniques.[16-17] An oxidant is used to polymerize the monomer and anions are doped as a counter part of the oxidative CP. This method to produce ICPs is widely used in industry. [18]

Electrochemical synthesis

The conducting polymers are also synthesized by electrochemical methods. It is very simple and better technique for preparation of conducting polymers because in this technique,

polymerization and doping level could be controlled. In this technique three electrodes working, counter, and reference electrode are required. The physical properties of CPs coating are affected by the nature and size of counter ions used. [19] Polyaniline composites doped with tungstate and molybdate were synthesized by electrochemical method.

2.3 Dooping

During the doping process, an organic polymer, either an insulator or semiconductor having a small conductivity, typically in the range 10–10 to 10¹ S/cm, is converted to a polymer which is in the ‘metallic’ conducting regime (–1 to 10⁴ S/cm). The controlled addition of known, usually small (10 per cent) non stoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer.

3. Experimental technique

3.1. Chemical method

In chemical synthesis, there are three reactants of PANI that require aniline, oxidant, and acidic medium. HCl and H₂SO₄ are common acids used in the synthesis of PANI. The oxidant polymerization method is the most communal mechanism used to synthesize PANI, while aniline reacts with an acidic substance as a neutralizing agent and polymerizes by adding one drop of an oxidizing agent such as ammonium persulfate (APS) at dissimilar temperatures. After realization, the polymerization mechanism (3 h) was an aqueous solution separated by filtration. Pure PANI can be obtained by rinsing the above solution 5–6 times with deionized water. Alcohol and acetone are then added to make the filter colorless and ensure that non-reactive materials

are completely removed. The product is slime green and is well-known as PANI polyemeraldine salt, which is unstable due to the existence of swords. Hence, the polyemeraldine salt converts to the PANI-EB structure, which is naturally stable at room temperature, allowing this precipitate to equilibrate with an appropriate amount of NH_4OH .

3.2. Electrochemical method

The PANi obtained from the electropolymerization (ECS- PANi) has somewhat lower conductivity, higher solubility, lower crystallinity, higher band energy, structure with higher benzenoid rings and higher size than that of the chemically synthesized PANi (CS-PANi).

3.2.1 Electrochemical measurements

Electrochemical cell setup

The electrochemical cell (15 ml capacity) was made of glass. The teflon made cell top encompasses three separate openings for the insertion of electrodes viz. working electrode, counter electrode and reference electrode. The cell top also has the purging and blanketing facilities for purging nitrogen gas to remove dissolved oxygen.

Reference and counter electrodes

Ag/AgCl was used as reference electrode. The reference electrode consists of silver wire (F=1mm and 10cm length) electrochemically coated with AgCl, placed in a teflon tube with 0.1M KCl aqueous solution. The standard electrode potential of Ag/AgCl (0.1M KCl) is found to be +0.288 V (vs. NHE) with SD of 0.013 V at 25°C. A platinum foil of 1x1 cm^2 was used as counter electrode. Pt electrode was cleaned with dilute detergent solution, isopropyl alcohol and sodium hydroxide solution. Finally, it was rinsed with DI water.

3.2.3. Working Electrodes

Glassy carbon electrode

The glassy carbon electrode (GCE) of geometric area 0.0314 cm^2 was used as working electrode. Well established procedure for the pre-treatment of GCE were adopted. First the electrode was rinsed with water-ethanol-ammonia mixture followed by ethanol-ammonia, ethanol-acetic acid and ethyl acetate-ethanol mixture. It was then washed thoroughly with distilled water and trichloroethylene. By this protocol the oxide layers, surface active and organic compounds that were adsorbed onto GCE surface were removed. When the electrode surface was seriously contaminated, the most effective and at the same time the simplest way employed for the removal of the contamination from the surface is to rub the electrode with the fine powder of 0.05 mm Al_2O_3 . After rubbing, the electrode is wiped with a filter paper and then rinsed with DI water. The fine particles of alumina adsorbed on GCE were removed by ultrasonication. Freshly polished and cleaned GCE showed reversible redox behaviour. This was ascertained by performing CV of Ferro/Ferri system. In order to get reproducible results great care was exercised in the electrode pre-treatment. The electrochemical active surface area of the electrode was determined by recording current-potential curve for potassium ferrocyanide. The active surface area was calculated from the following equation.

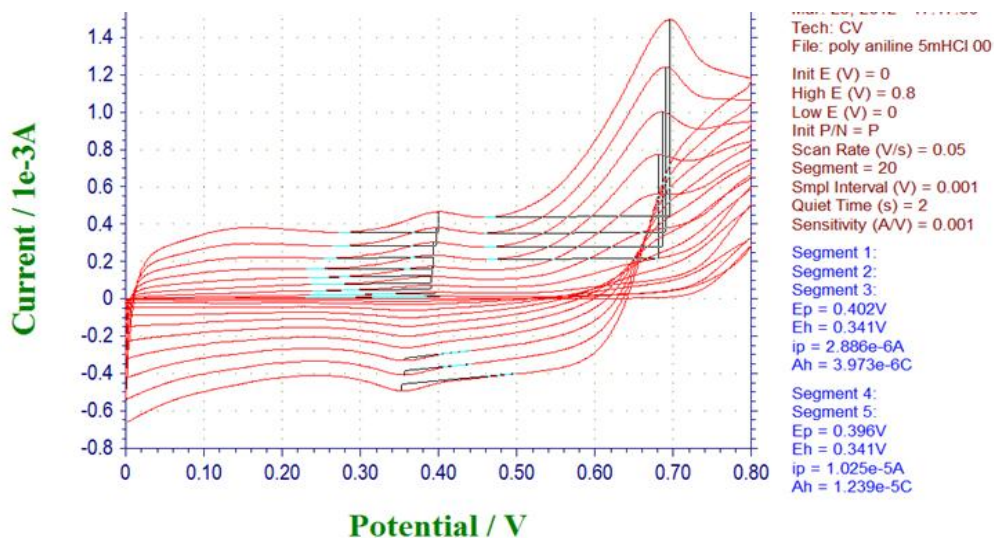
$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C_0$$

Where i_p is peak current in A, n is number of electrons transferred, A is area of the working electrode in cm^2 , D is diffusion coefficient in $\text{cm}^2 \cdot \text{s}^{-1}$, is scan rate in $\text{V} \cdot \text{s}^{-1}$ and C_0 is the concentration of ferrocyanide solution in mM.

Atomic Force Microscopy

The surface morphology of the electrode surfaces was analysed using Nanosurf Easy Scan 2 Atomic Force Microscopy in the non-contact mode to get 2D, 3D images, size distribution graph and surface roughness data were extracted.

3.3. Preparation of poly aniline:



Electrochemical studies of reactive dye blue 4 [RB 4]

Reactive Blue 4

Molecular Formula: C₂₃H₁₂Cl₂N₆Na₂O₈S₂

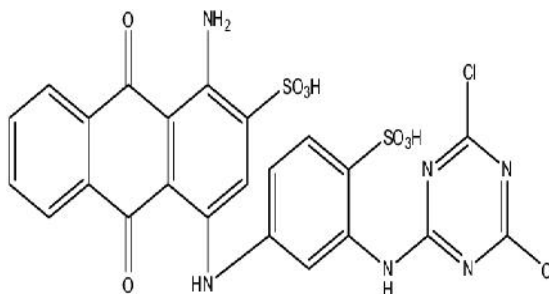
Molecular Weight: 681.39

CAS Registry Number: 13324-20-4/4499-01-8

Manufacturing Methods : 1-Amino-4-bromo-9,10-dioxo-9,10-dihydroanthracene-2-sulfonic acid and 2,4-Diaminobenzenesulfonic

acid condensation, and 2,4,6-Trichloro-1,3,5-triazine condensation and salting-out.

Properties and Applications: bright blue. Dark blue powder. The strong sulfuric acid for red brown, diluted into blue; In nitric acid to orange, no change after diluted. The dye water solution is blue, with 1 Moore sodium hydroxide solution is still blue, continue to join insurance powder and warm, turn dark red, plus a boric acid to red,. Mainly used for cotton, nylon, wool, silk and viscose yarn and fabric as the dyeing and printing, printing and dyeing directly.



3.3.1. Cyclic voltametric behaviour

The cyclic voltametric behaviour of RB 4 was studied at different pH, scan rates, and concentrations using glassy carbon electrode (GCE) and the respective cyclic voltammograms

were recorded. The effect of pH was studied by measuring and comparing the peak potentials and current. The detailed studies related to the influence of scan rate and concentration were also carried out.

3.3.2. Effect of pH

Since there was characteristic effect from pH 1.0, the cyclic voltammetric studies of RB 4 were carried out in the pH range 1.0 to 13.0 and five representative pHs were chosen for study. At all pH viz. 1.0, 4.0, 7.0, 9.0 and 13.0, two anodic peaks and one cathodic peak in the reverse scan were observed. Of the two peaks, anodic peak II around 700-900mV showed prominence with higher current in the pH range 1.0 to 13.0. The other anodic peak and cathodic peak lost their sharpness when the pH was increased. Hence the anodic peak II was considered for further studies to probe the oxidation mechanism. For the study

of influence of pH on the cyclic voltammetric response, five pH viz 1.0 4.0, 7.0, 9.0 and 13.0 were chosen and the cyclic voltammograms were recorded for 200 ppm of RB 4 at a scan rate of 100 mV/s. The peak currents and peak potentials were plotted against pH and the plots are given in figures 3.1.1 & 3.1.2. The maximum peak current response was found in pH 7.0. This is due to faster electron transfer at acid pH 7.0 and indicates that the electrochemical oxidation of RB 49 is facilitated in neutral media. Hence it can be considered as an optimum pH for the study of RB 49. The peak potential also decreased with increase in pH. The peak potential of anodic peak II shifted anodically with pH whereas that of cathodic peak shifted cathodically with pH.

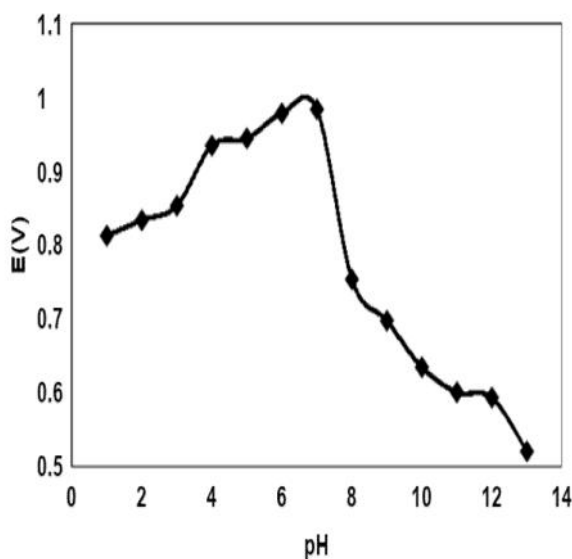


Fig 3.1.1 Curve of peak potential Vs pH for RB4

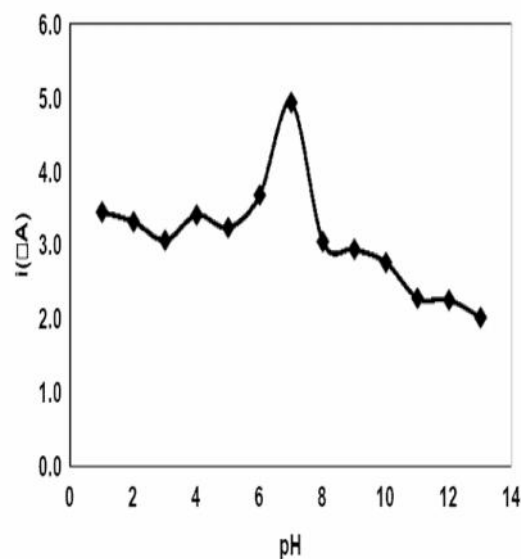


Fig.3.1.2 Peak current Vs pH for RB4

4. Results and Discussion

4.1. Cyclic voltammetric studies of RB 4 at pH 7.0

The peak currents and peak potentials from the cyclic voltammograms obtained for 100 ppm RB 4 at different scan rates and different concentrations were listed in table 3.1.1 As an illustration, the cyclic voltammogram obtained for RB 4 at this pH is shown in figure 3.1.3. The two anodic peaks were observed at the potential around -250mV (Peak I), 750 mV (Peak II) and three cathodic peaks were observed at the

potential around at 400mV (Peak III), -750mV (Peak IV), -800mV (Peak V). With the increase in the scan rate from 25 to 300 mV/s, the anodic peak potential shifted anodically and the cathodic peak potential shifted cathodically. The anodic peak with high current response was considered for further studies. The plot of peak current versus scan rate was given in fig 3.1.4. The straight line plot of peak current versus square root of scan rate ($R^2 = 0.9778$) was given in fig.3.1.5. The logarithmic plot of peak current versus scan rate is given in fig.3.1.6. The slope value of the plot was 0.676. These all facts indicated the adsorption-controlled oxidation of RB 4. The

anodic peak and cathodic peak did not satisfy the reversibility criteria. The fractional n value (0.6378) calculated from the plot of peak potential versus log scan rate (Fig.3.1.7) indicated the irreversibility of the reaction. By varying the concentration of the substrate from 100 to 500

ppm, the cyclic voltammetric behaviour at 100 mV/s scan rate was studied. The linear plot of peak current versus concentration (Fig.3.1.8) showed the linearity between both. The peak potential also increased with the concentration.

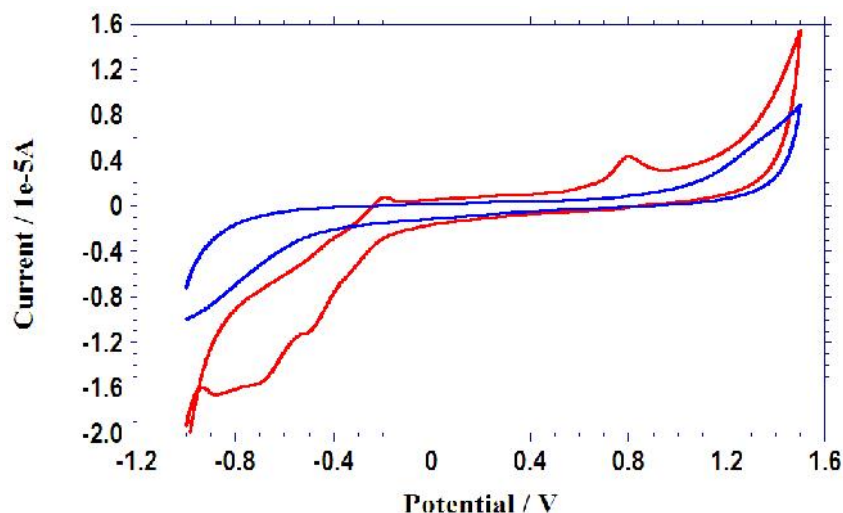


Fig 3.1.3.Cyclic Voltammograms of RB 4 recorded at (a) GCE and (b) GCE/ PANI in pH 7

Table 3.1.1: Peak potential and peak current data extract from CV recorded for RB 4 in pH 7

□ (mV/s)	oxidation peaks				Reduction peaks					
	peak I		peak II		peak III		peak IV		peak V	
	-E(V)	i(μA)	E(V)	i(μA)	-E(V)	i(μA)	-E(V)	i(μA)	-E(V)	i(μA)
25	0.1556	0.140	0.7393	1.297	0.4135	2.223	0.7261	2.814	0.7124	4.221
50	0.1837	0.441	0.7831	2.192	0.4365	4.251	0.7531	6.141	0.8351	8.321
75	0.1875	0.911	0.7991	3.271	0.4541	6.502	0.7541	9.368	0.8541	12.32
100	0.1967	1.334	0.8132	3.452	0.4932	10.254	0.7596	12.595	0.8841	16.350
150	0.2053	2.435	0.8198	5.152	0.4958	12.505	0.7651	15.822	0.8882	20.550
200	0.2018	2.735	0.8234	5.235	0.4964	15.206	0.7706	19.049	0.8941	24.639
250	0.2214	3.804	0.8339	6.630	0.5012	17.908	0.7761	22.276	0.8962	28.727
300	0.2255	4.273	0.8423	7.584	0.5112	20.609	0.7911	24.503	0.8984	31.816

5. Conclusion

This chapter discusses the results obtained from the electrochemical studies of selected Reactive Blue 4 at glassy carbon electrode with PANI (GCE/PANI). The cyclic voltammetric of RB 4 was studied at different scan rates, concentrations and pH at (GCE/PANI). The effect of pH was studied by measuring and comparing the peak potentials and current. The influence of pH on CV of 200 ppm RB 4 at 100 mV/sec scan rate was studied. RB 4 exhibit characteristic response in the acidic, neutral and basic pH media. The studies were carried out in the pH region 1.0 to 13.0. In all the pH ranges studied, one predominant anodic peak and a good cathodic peak in the reverse scan were observed. In all these cases, the intense and sharp anodic peak appeared in the region 700-900 mV. Due to the high current, the anodic peak in the above region was considered for comparisons. From these studies, the anodic current increase in pH up to pH 7.0 then slowly decreased in basic medium. This indicates that the rate of oxidation of RB4 is decreased in basic pHs. It is concluded that pH 7.0 is the most suitable pH for analytical studies due to maximum peak current. The effect of scan rate was studied from 25 to 300 mV/s in pH 7.0 for 200 ppm RB 4. The plots of peak current versus scan rate, square root of scan rate and the logarithmic plot of current versus scan rate were made. The anodic peak potential shifts anodically with the increase in scan rate. All the above facts revealed that the oxidation of RB 4 at pH 7.0 was irreversible and adsorption-controlled and ensure the trace level detection with conducting polymer (GCE/PANI) modified electrode.

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