

Synthesis and Electrochemical studies of Polyaniline at Different Atmospheric Condition

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Abstract:- Electroconducting polyaniline (PAni) are of great interest for a large number of applications due to their easy processing and relatively low cost compared to other materials such as the inorganic one. The PAni was synthesized by bulk polymerization of aniline using 0.25M potassium perdisulfate ($K_2S_2O_8$) as an oxidant at room temperature, in 1M hydrochloric acid medium. The Cyclic Voltammetric studies (CVs) are obtained in 1.0 M H_2SO_4 electrolyte by casting the PAni paste on GC working electrode. The effect of pH on the voltammetric response is studied to determine the electroactive behaviour of PAni modified GCE in redox reactions over a pH range of 1.0 to 13.0. CVs of PAni modified GCE were performed under different atmospheric conditions (deareated, O_2 & N_2) in the pH 1.0. The surface coverage values as well as the diffusion coefficient values are found from Chronoamperograms of the PAni modified GCE by Cyclic voltammetric method. PAni modified GCE enhances the electrocatalytic activity towards methanol reduction for N_2 saturated buffer. The double layer capacitance value calculated from Electrochemical Impedance Spectroscopy.

Key Words: Chronoamperometry, Cyclic voltammetry, Electrochemical Impedance Spectroscopy, PAni

I. INTRODUCTION

Among the conducting polymers, polyaniline (PAni) generates most attention because it has the highest specific capacitance due to multi-redox reactions, good electronic properties due to protonation [1], and low cost for its infinite abundance. Moreover, it has better thermal stability and can be easily synthesized by chemical or electrochemical methods. PAni can be employed as the carbon precursor to fabricate metal free non-precious catalysts [2], because of its high content of nitrogen, which may play important role in enhanced electrochemical activity. The aim of this work is to discuss the role of different atmosphere and catalytic activity in determining the electrochemical characteristics of conducting polymers, with particular emphasis on polyaniline.

II. EXPERIMENTAL DETAILS

Instrumentation

The polymer was characterized by various instrumental techniques. For recording the UV-vis absorption spectra, a computer controlled Jasco V-530 spectrophotometer was used. The morphology of the polymer and polymer-ceramic nanocomposites has been studied by Scanning Electron Microscopy (SEM) method. Scanning electron micrograms were obtained using Model: JEOL JSM 6360. Electrochemical workstation CHI 650C (CH Instruments, USA) was employed for the various electrochemical studies performed.

Cell setup

The cell was made of glass, having a capacity of 15ml and the teflon lid with four separate holes for the gas purging and three electrodes viz. working electrode, counter electrode and reference electrode. The cell setup was kept in a Faraday cage. The cell top also had the purging and blanketing facilities for nitrogen and oxygen gas with separate tubes to remove any other gas. Pt was used as counter electrode and silver-silver chloride electrode as reference electrode. Nitrogen (N_2) and Oxygen (O_2) gases were used in these electrochemical studies. In these studies, the normal condition (without saturated buffer with any other gases) was changed by passing N_2 or O_2 gas three minutes continuously into the buffer solution through the top of the cell using a very small tube. During the process, the tube was removed from the solution and was maintained above the solution until the process got completed.

Reagents and Chemicals Used

Aniline was obtained from M/S sigma Aldrich, potassium perdisulphate, hydrochloric acid (Merck 98 %), Sodium hydrogen phosphate, citric acid, phosphorous acid and sodium hydroxide (Sigma-Aldrich Co) were used as such.

Synthesis of Poly aniline

Aniline (0.1M), potassium perdisulphate (0.25M) and 1M hydrochloric acid were made upto 200ml using conductivity water. The solution was kept stirred for 3hrs with the help of a magnetic stirrer at room temperature, it was kept overnight in the refrigerator, after which the dark green powdered obtained was filtered and dried. The

solubility of PANi was tested and was found to be soluble in dimethyl sulphoxide and dimethyl formamide.

III. RESULTS AND DISCUSSIONS

This part of the results and discussion deals spectral details, redox and electrocatalytic behaviour of conducting polyaniline.

A. UV – Vis Studies of Polyaniline

Comparing the obtained results from Fig. 1, it was found that both the transitions were observed at 310 nm because of π - π^* transition and a broad peak from 500 to 800 nm centered on 610 nm is due to the excitation formation of quinonoid ring corresponding to the semiconducting phase of PANi-H₂SO₄. This may be probably due to its unique chemical structure and degree of ionization.

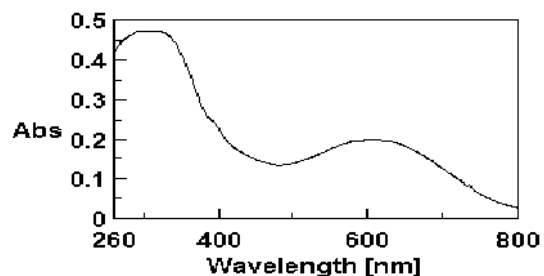


Fig. 1. UV-Vis of PANi

B. SEM And Edax of Polyaniline

Morphology of PANi was studied, using Scanning Electron Microscope (SEM) and is shown in Fig. 2. As can be seen in Fig, homogeneous pebbles were obtained when potassium persulfate was used as oxidant. This is in good agreement with previous reports on the morphology of PANi [3].

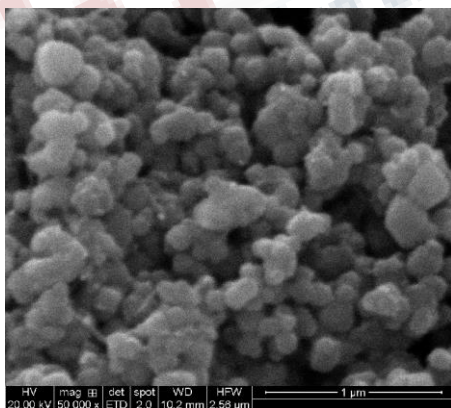


Fig. 2. SEM images of PANi

IV. ELECTROCHEMICAL CHARACTERIZATION OF POLY ANILINE

A. Cyclic Voltammetry

Voltammetric studies of PANi modified GCE were performed under normal as well as nitrogen and oxygen saturated conditions in the pH range of 1.0 to 13.0. The CVs were obtained in 1.0 M H₂SO₄ electrolyte by casting the PANi paste on GC working electrode and scanned between -1.2 to 1.2 V with scan rates ranging between 50 to 500 mV/s.

B. Working Electrode Preparation:

PANi modified glassy carbon electrodes (PANi/GCE) was employed in the present investigation. It was dissolved in dimethyl sulfoxide (DMSO) to form PANi solution. PANi film was produced by casting PANi solutions (1 drop) onto a clean and pre-treated 0.0314cm² GCE and then allowing the solvent to evaporate. They were consequently rinsed with water and then transferred to an electrochemical cell for experimental purpose. A three electrode cell with a saturated calomel reference electrode (SCE), a platinum wire counter electrode, and PANi modified glassy carbon working electrode were employed. All electrochemical experiments were carried out at a thermostatic temperature of 25.0 ± 2°C.

C. Influence of pH

The effect of pH on the voltammetric response was studied to determine the electroactive behaviour of PANi modified GCE in redox reactions over a pH range of 1.0 to 13.0, using pH buffer solutions adjusted to the desired condition. As a result, the redox peaks became smaller as pH was increased from 1.0 to 6.0. It protonates and deprotonates the base (-NH-) sites in PANi leading to switching of PANi between oxidation states [4]. This means that there is a pH dependence of the oxidation states of PANi. When the pH of the polymerisation reaction is greater than six, PANi becomes non-electroactive. The loss of its electroactivity is due to the failure of the formation of the Emeraldine salt (ES) salt. The optimum pH range for good sensitivity response appeared to be pH 1.0. So pH1 was chosen for further electrochemical studies.

The switching of oxidation states and optical properties of PANi are interlinked and influence each other directly. The tendency of PANi to switch between oxidation states directly influences its UV-vis absorption characteristics [5]. The electrochemical switching of polyaniline between oxidation states can be readily monitored by Cyclic Voltammetry and it is to be observed at different atmospheric condition.

D. Effect Of Different Atmosphere

Cyclic Voltammograms for PANi modified GCE at pH 1 was carried out in normal (deaerated buffer) as well as N₂ and O₂ saturated buffer and compared with the bare GCE. This voltammogram has been demonstrated in Fig.3. Cyclic voltammogram depicts well-defined oxidation-reduction (redox) peaks observed at 50 mV/s.

The PANi modified GCE (Fig.3) at pH 1 shows oxidation and reduction peaks at 619.5mV and 205.3mV respectively in the normal condition. It can be ascribed to the redox between emeraldine base to pernigraniline. It shows good electrical conductivity [6]. It shows an oxidation peak at 648.8mV and a reduction peak at 198.3mV in N₂ saturated buffer. The Voltammogram under O₂ saturated buffer depicts an oxidation peak at 705mV and a reduction peak at 183.7mV. The results clearly show that N₂ and O₂ saturated buffer could reduce the current peak and the oxidation potential is shifted more positive and the negative potential is shifted more negative. Thus, the oxygen reduction ability was observed at pH 1 and at very low potential. It exhibits a good electrocatalytic activity making it applicable in fuel cells.

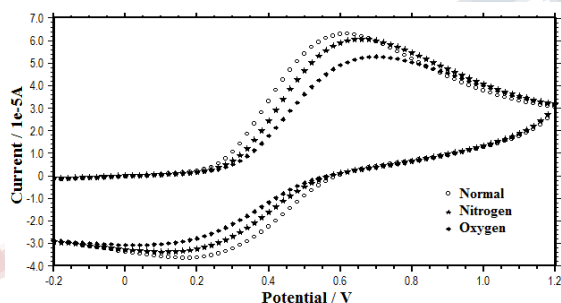


Fig. 3. Cyclic voltammetric responses obtained for PANi modified GCE with a scan rate of 50 mV/s at pH1

E. Chronoamperometry Studies of Poly aniline

Double potential-step chronoamperometric studies was performed on GCEs modified with PANi in the absence and presence of N₂ and O₂ saturated buffer with an initial and final potential of -1.4 to 1.2 V versus GCE. Chronoamperograms of the PANi modified GCE immersed in 1.0 M H₂SO₄ at 25±2°C for 2 s. Observed monotonous rising current in the presence and absence of N₂ and O₂ saturated buffer. The rise in the current is high in the normal condition when compared with that of N₂ and O₂ saturated buffer.

Using the slope values of I vs t^{-1/2}, the diffusion coefficient values of PANi modified GCE was determined using the Cottrell equation.

$$I = nFD^{1/2}AC_p\pi^{-1/2}t^{-1/2} \quad (1)$$

$$\text{Slope} = nFD^{1/2}AC_p\pi^{-1/2} \quad (2)$$

Here, C_p (mol cm⁻³) is the concentration of the electroactive PANi in 1.0 M H₂SO₄, D (cm²s⁻¹) is the diffusion coefficient of PANi in 1.0 M H₂SO₄, and A (cm²) is the geometric area of the GC electrode. The concentration of the electroactive species, C_p [7] was determined using the relation C_p = N_p / Al, where N_p is the amount of electroactive species on the surface of the PANi modified electrode and l is the film thickness. The surface coverage of the electroactive species, (N_p) was determined from cyclic voltammograms at low scan rates (50 mVs⁻¹) using the relation N_p = Q / nFA, Where Q is the charge consumed, n is the number of electrons involved in the reduction of the catalyst, and F is the Faraday constant(96485 C mol⁻¹). The slope values are taken from the chronoamperometric curves. It is noteworthy that, the surface coverage (N_p) values obtained are 1.2523x10⁻⁸, 2.896x10⁻⁸ and 6.007x10⁻⁸ and the diffusion coefficient values are 5.237x10⁻⁷, 7.876x10⁻⁷ and 1.567x10⁻⁸ under normal, N₂ and O₂ saturated buffer respectively.

In diffusion coefficient value is slightly higher than the literature value (Manoj K. Ram et al.,) [8] under normal condition. Thus, the surface coverage values as well as the diffusion coefficient values are found to decrease from normal - O₂ saturated buffer.

F. Effect of pH in presence of Methanol

Linear Sweep Voltammograms (LSV) (Fig.4) have been recorded in the presence of 1.0M H₂SO₄ and 1.0M MeOH (acidic methanol), on PANi modified GCE to observe the enhancing catalytic activity towards methanol reduction. It was carried out in normal as well as N₂ and O₂ saturated buffer at 50 mV/s. It shows a reduction peak at 248.1mV under normal condition. Amazingly, this PANi emeraldine base form transformed to the leucoemeraldine base and it goes to a more reducing form, characterized by an associated small current density. This aspect gives an indication of the presence of a strong reducing chemical species on the polymer surface [9]. It is obvious that it can be used in Direct Methanol Fuel Cells (DMFC) and proton exchange membrane (PEM) fuel cells [10].

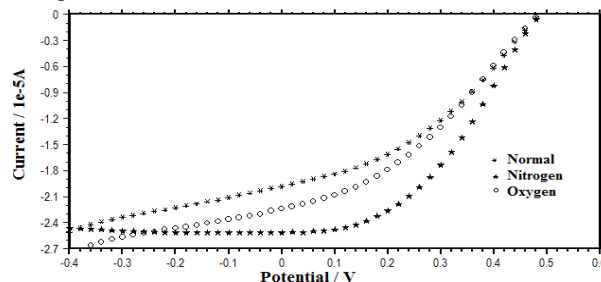


Fig. 4 Linear Sweep Voltammetric cathodic peak responses obtained for PANi modified GCE in presence of acidic methanol.

Interestingly, a reduction peak shifted slightly towards negative side at 180.3mV in N₂ saturated buffer. Under O₂ saturated buffer, a reduction peak at 162.4mV was observed. A high current at low potential of Oxygen Reduction Reaction (ORR) was observed at N₂ saturated buffer than that for O₂ saturated buffer. Thus, PANi modified GCE enhances the electrocatalytic activity towards methanol reduction for N₂ saturated buffer than when used under other conditions.

G. Electrochemical Impedance Spectroscopy of Poly aniline

EIS depicts the electrochemical impedance spectra for PANi modified GCE in 1.0 M H₂SO₄. The radius of semicircle is 2.365x10⁴ which is equal to charge transfer resistance. The double layer capacitance is calculated from equation 1 where resistance is derived from the low and high frequency resistance values.

$$C_{dl} = 1 / 2\pi f_{max} R_{ct} \quad (3)$$

The double layer capacitance value thus obtained is 5.6844 x 10⁻¹⁰ which is indicative of its high resistance.

CONCLUSION

PAni was successfully synthesized and characterized by UV and SEM. UV show that the polymerisation of aniline resulted in the π-π* transition and quinonoid ring system. SEM study shows the amorphous morphology of the polymer. The polymer was coated as a thin- film over GCE to produce PANi modified GC electrode. At pH 1.0, PANi modified GCE showed high current value in normal condition and N₂ and O₂ saturated buffer solution reduces the current and the reduction potential shifted towards negative side. O₂ and N₂ gases interfere into the polymer layer to decrease the charge at reduction and has been confirmed by Cyclic voltammetry and Chronoamperometric techniques. The Electrocatalytic behaviour observed for PANi modified GCE in the mixed solution of Methanol and Acid was worth proving it to be an electrocatalyst and enhancing the catalytic activity in N₂ saturated buffer.

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