

Electrocatalysis Of Insitu Polyaniline For Speed Up Of Redox Reaction At Electrode Surface

Mary Gojeh^{1,2}, Tesfaye Rafera², Micheal Onwumere³, Yilleng Moses Titus¹,
Gideon Wyasu¹

¹ Department of Chemistry, Faculty of Science, Kaduna State University, Kaduna, Nigeria

² Department of Chemistry, Faculty of Natural Science, Jimma University, Ethiopia

³ Department of Physics, Faculty of Science, Kaduna State University, Kaduna, Nigeria

Abstract : Polyaniline carbon paste electrode prepared by mixing polyaniline, paraffin, graphite powder and potassium ferrocyanide a known probe in electroanalysis was analysed. The ratio of polyaniline, paraffin and graphite for the construction of the electrodes and the effect of the concentration of this conducting polymer provides enormous opportunities for electrodes modification, rapid electron transfer and direct communication to produce a range of analytical signals and new analytical applications were studied. These modified electrodes exhibited an increase in surface area and speed up of redox reaction (Bare- 0.014 cm², Polyaniline- 0.028 cm²). Efforts have been made to discuss and explore various characteristics of PANI responsible for direct electron transfer leading towards fabrication of mediator-less sensors and electrodes reproducibility.

Keywords: Electrocatalysis, Polyaniline, Carbon Paste Electrode, Cyclic Voltammetry, Potassium ferrocyanide

I. Introduction

Electrocatalysis is a special field in Electrochemistry that has gained a special growth due to the application of new hybrid techniques. The application of new concepts of electrocatalysis for electrochemical processes has appeared as a necessity and not only attracting attention for chemists but for engineers. Many interpretations of electrocatalysis is due to electrochemical reaction with an adsorbed species, either as reactant and/or product, which can change the kinetics of the reaction [1]. One of the most important features of electrocatalysis arises from the different electrode kinetics using different polymers for the electrode surface.

Because of the simple preparation and easy renewal of the surface, carbon has been used extensively as a working electrode for a variety of electrochemical applications. Among the carbon electrodes, the carbon paste electrode (CPE) is of particular importance because its ease and speed of preparation and of obtaining a new reproducible surface, the low residual current, porous surface and low cost are some advantages of CPEs over all other carbon electrodes. Therefore, the CPE can provide a suitable electrode substrate for preparation of modified electrodes [1, 2].

Modifier such as polyaniline has captured attention of scientific community due to the discovery of its high conductivity and low cost. Therefore researchers are continuously exploring its applications because of a number of useful features such as direct and easy deposition on the sensor electrode, control of thickness, redox conductivity and polyelectrolyte characteristics, high surface area, chemical specificities, long term environmental stability and tuneable properties. PANI is an interesting material for sensor interfaces because it can act as an effective mediator for electron transfer in redox reactions [3]. PANI is considered to be an attractive polymer since it exhibits two redox couples in right potential range to facilitate charge transfer and thereby acts as self-contained electron transfer mediator [4].

This paper presents a carbon paste electrode as the working electrode and voltammetry experiment resulting to current measured as a function of potential and electroanalytical chemistry stems from the use of voltammetry to obtain analytical (e.g., concentration), thermodynamic (e.g., redox potentials and equilibrium constants), kinetic (e.g., rate constants for reactions involving electrogenerated species) and mechanistic information about chemical systems in which redox chemistry plays a role were made.

II. Experimental

2.1. Materials

Ammonium persulfate (NH₄)₂S₂O₈, 98% Sigma Aldrich), hydrochloric acid (HCl, 35%, Alpha), sulfuric acid (H₂SO₄, 98%, Fisher chemicals), potassium nitrite (KNO₂, 99%, Qualikems), aniline (C₆H₅NH₂, 100%, Sigma Aldrich) and Potassium Ferrocyanide were used as received without any other treatment. Aqueous solutions were prepared with deionized water. In this study, the following chemicals were used as received.

2.2. Preparation of Polyaniline powder

Polyaniline was prepared by adopting the method [5] with some modifications. Aqueous solution of ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) of 100 mL of 0.25 M was prepared. Then 2 mL of 0.20 M solution of aniline was added in 8.15 mL of 1 M hydrochloric acid (HCl) (aniline hydrochloride) and dissolved in distilled water in a volumetric flask to 100 ml of solution. Both solutions were kept for 1 h at room temperature ($\sim 25\text{-}30^\circ\text{C}$), then mixed in a beaker, briefly stirred, and left at rest to polymerize.

Polymerization was allowed overnight in a refrigerator at 5°C . The green precipitate that formed was removed by filtration, washed with 1M HCl followed by acetone until clear filtrate was obtained. The obtained polymer was dried in air and then vacuumed desiccator for 24 hours at room temperature of (30°C). The green material obtained was identified as the emeraldine hydrochloride.

2.3. Preparation of Insitu PANI modified carbon paste electrode

To prepare Insitu PANI CPE, several concentrations (120, 140, 160, 180, 200, 220 and 240 mg) PANI powder was mixed with graphite powder (800 mg) and (100 μL) paraffin oil. Mixture was transferred to the mortar and pestle and then homogenized by adding 2.0 ml of dichloromethane and mixed thoroughly. The solvent was evaporated at room temperature (for 24 h). The resulting composite electrode assembly was done by filling the open tip of plastic (diameter of 2.4 mm) until thoroughly packed to have electric contact with copper wire. The paste was smoothed with a paper to produce a reproducible working surface. For comparative analysis, a surface PANI deposited electrodes were prepared alongside insitu PANI electrodes [5].

2.4. Electrodeposition of Polyaniline

Electropolymerisation was carried out by mixing 2.5 ml of 0.25 M of ammonium persulfate aqueous solution with 2.5 ml of 1M aniline hydrochloride in a vial. Cyclic voltammometry at potential between -0.2 and 1.0 V, on carbon paste electrode vs. Ag/AgCl electrode at a scan rate of 50 mV in 5 cycles was carried out, taking several successive scans [6]

2.5. Electrochemical Measurements

Epsilon (BASI) was used to carry out all electrochemical measurements. A conventional three-electrode setup was used with the CPE electrode as the working electrode and a platinum wire as a counter electrode ((1 mm) mw 4130. An Ag/AgCl (Thermo Scientific Orion Model Number: 900011) served as a reference electrode. All potentials were reported with respect to this reference electrode.

III. Result And Discussion

3.1. Characterization of Insitu and Surface Polyaniline Modified Carbon Paste Electrodes

3.1.1. Insitu and Surface Polyaniline Modified Carbon Paste Electrodes

PANI-modified CPE was prepared using two approaches: the Insitu PANI modification of CPE with PANI where the PANI was synthesized and incorporated to carbon paste and the other approach is electropolymerization of the PANI on a CPE surface. The two electrodes made from different modification approaches were characterized by cyclic voltammometry in 0.5 mM H_2SO_4 electrolyte solution. Fig 1 is for the Insitu modified PANI modified CPE whereas Fig 2 is the electropolymerized PANI modified CPE. The voltammogram shows some basic information like the features of the PANI reduction and oxidation. The oxidation and reduction peak potentials of PANI at CPE were found to be at 0.3, 0.6, 0.1 and 0.4 V respectively of which were in accordance with other [6]

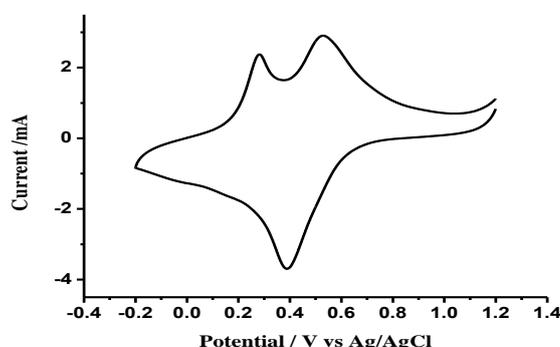


Fig 1: Cyclic voltammometry for Insitu PANI modified electrode in 0.5 mM H_2SO_4 at scan rate 100 mVs^{-1} between potentials of -0.4 V and 1.4 V

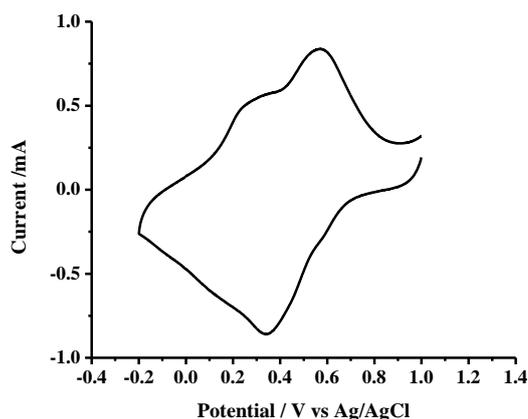


Fig 2: Cyclic volttermmetry for surface PANI modified electrode in 0.5 mM H₂SO₄ at scan rate 100 mVs⁻¹ between potentials of -0.4 and 1.4 V.

3.2 Effect of PANI concentration

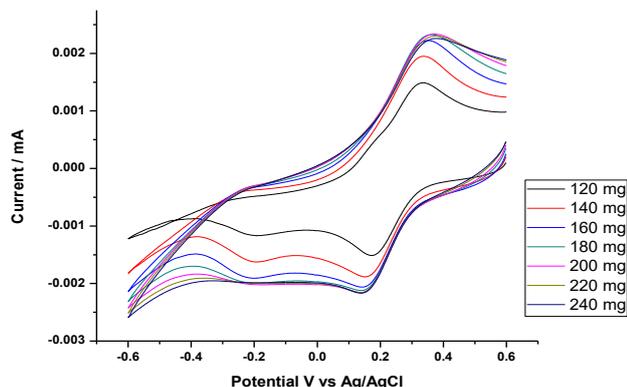


Fig 3: Cyclic Voltammogram of Effect of concentration of PANI in 0.1M K₃Fe(CN)₆ in a 1M supporting electrolyte of KNO₃ at PANI CPEs at a scan rate of 20 mVs⁻¹

Studying the concentration at which PANI as in Fig 3 was found more electroactive gives the work specific focused area. Concentration of PANI at 200 mg which was moderate for the proportion of mixture, not scanty to indifferent and not too much to insulate was found to have a higher current response and decreases overpotential which is in accord with [7]

3.3. Effect of Scan rate

Since the bare electrode was found to have a sluggish kinetic the rate of electron transfer of the PANI modified electrode was studied and at 20 mVs⁻¹, the rate was found to exhibit an impressing decrease in redox potential of the K₃Fe(CN)₆ and a high increase in redox current response as shown in Fig 4.

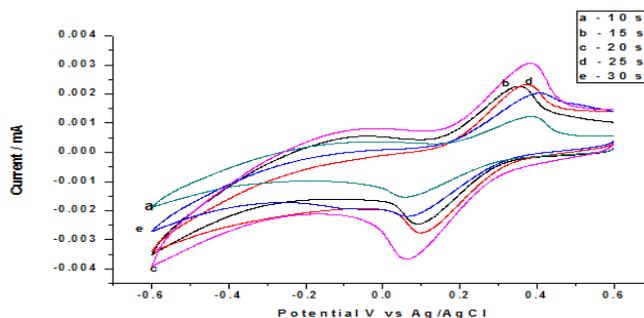


Fig 4: Cyclic Voltammogram of Effect of scan rate in 0.1M K₃Fe(CN)₆ in a 1M supporting electrolyte of KNO₃ at PANI CPEs

3.4 Determination of the active surface area of the prepared electrode

The active surface area of the prepared CPE was determined by the Randle-Sevcik relationship that considers an electrode reaction in which the rate is governed by diffusion of the electroactive species to a planar electrode surface. The peak current, I_p , is related to area of the electrodes as:

$$I_p = k n^{3/2} A D^{1/2} C^b \nu^{1/2}$$

Where the constant $k = 2.7 \times 10^5$

n = number of moles of electrons transferred per mole of electroactive species

A = area of the electrode in cm^2

D = diffusion coefficient in cm^2/s

C^b = solution concentration in mole/L

ν = scan rate of the potential in volt/s.

I_p = linearly proportional to the bulk concentration C^b , of the electroactive species, and the square root of the scan rate, $\nu^{1/2}$.

Thus, a CV of scan rates at 10, 15, 20, 25, 30 and 35 mV/s^{-1} were run and a graph of the I_p vs. $\nu^{1/2}$ was plotted and the slope from the linear equation: $y = 2.58x - 0.1358$ (x in V/s), $r = 0.9999$ The calculated area was found to be 0.014 cm^2 for Bare electrode. In the same manner the active surface area of Surface PANI modified CPE, Insitu PANI modified CPE were also determined as shown in Table: 1.

Table 1: Summary of the electrode's surface area.

Surface area of bare CPE (cm^2)	Surface area of Surface PANI modified CPE (cm^2)	Surface area of Insitu PANI modified CPE (cm^2)
0.014	0.019	0.028

3.5 Comparative study of the working potentials of Bare, surface and Insitu CPEs

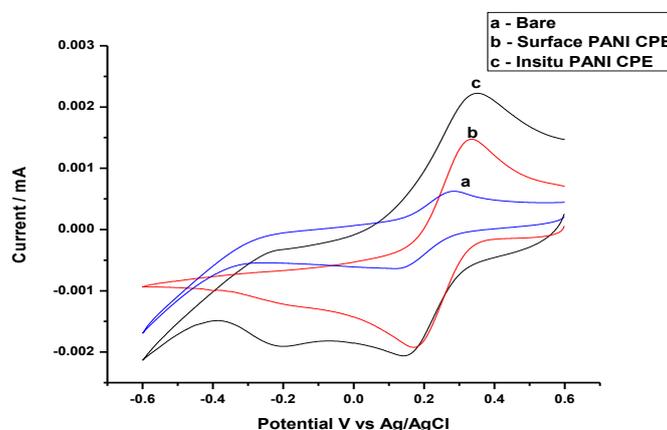


Fig 5: Cyclic Voltammogram of $0.1\text{M K}_3\text{Fe}(\text{CN})_6$ in a 1M supporting electrolyte of KNO_3 at (a) Bare (b) surface (c) Insitu PANI modified CPE at a scan rate of 20 mVs^{-1}

The electrode current response at Insitu PANI CPE were found to be higher than that in surface modified electrode that could be due to a higher surface area exhibited in the Insitu PANI modified electrode. The rate of electron transfer as increased with PANI which decreases the reduction (oxidation) potential of the $\text{K}_3\text{Fe}(\text{CN})_6$ by decreasing overpotential and increasing the redoxion (oxidation) current. This is in accordance with [7-10]

3.6. Repeatability Study

The repeatability of the preparation of the used electrodes (Bare, Surface, Insitu PANI modified electrodes) was evaluated by using several modified electrodes toward the detection of $0.1\text{M K}_3\text{Fe}(\text{CN})_6$ in a 1M supporting electrolyte of KNO_3 for 5 times on at interval of 5 days as shown in Fig 6 . The experimental result was found to be 3.2 ± 0.28 . No significant differences at the 95% confidence level were encountered. Thus, the repeatability of the three electrodes was acceptable

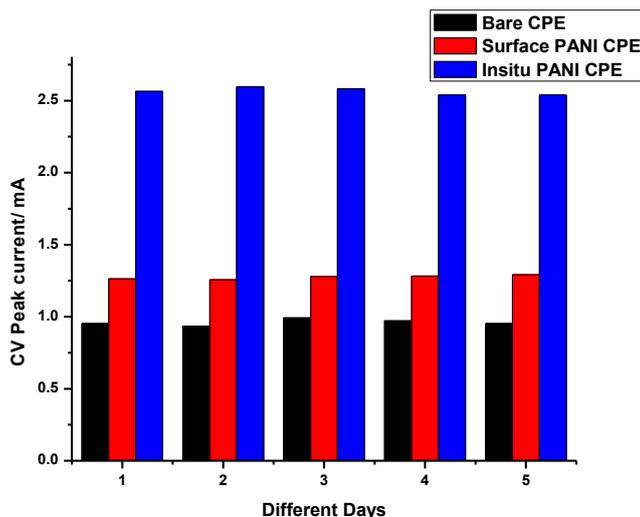


Fig 6: Repeatability study of the bare, Surface and Insitu PANI modified CPE towards 0.1M $K_3Fe(CN)_6$ in a 1M supporting electrolyte of KNO_3

IV. Conclusion

The sensor prepared using insitu polyaniline, based on acid doped-catalyzed synthesis of conducting PANI shows various remarkable characteristics of PANI like controllable conductivity, charge transfer capability, good processibility, environmental stability, mechanical flexibility for fabrication of variety of sensors and reduces the drawback of carbon paste electrodes for redox reactions. This provides a platform for analysis of various analytes.

Acknowledgement

The authors Appreciate the Department of chemistry, Jimma University, Ethiopia for providing the facilities and Bench Space for the research and also appreciate the financial support received from Prof. Lawrence Abraham Gojeh.

Reference

- [1]. S. Sharath Shankar, B.E. Kumara Swamy, M.Pandurangachar, Umesh Chandra, B.N. Chandrashekar, J.G.Manjunatha, B.S. Sherigara, *Int. J. Electrochem. Sci.*, 5 (2010) 944.
- [2]. R. Raghavendra Naik, E. Niranjana, B. E. Kumara Swamy, B. S. Sherigara, H. Jayadevappa, *Int. J. Electrochem. Sci.*, 3 (2008) 1574.
- [3]. Shi, L., Xiao, Y., Willner, I., 2004. *Electrochem. Commun.* 6, 1057–1060.
- [4]. Dhand, C., et al., Recent advances in polyaniline based biosensors. *Biosensors & Bioelectronics*, 2011(6): p. 2811-2821
- [5]. Kulkarni, M, Viswanath, A, Aiyer, R, Khanna, P: *J. Polym. Sci., Part B: Polym. Phys.* 43, 2161 (2005) Zhang, L., J. Zhang, and C. Zhang, Electrochemical synthesis of polyaniline nano-network on alpha-alanine functionalized glassy carbon electrode and its application for the direct electrochemistry of horse heart cytochrome c. *Biosensors & Bioelectronics*, 2009. 24(7): p. 2085-2090
- [6]. Bard, A.J; Faulkner, L.R. *Electrochemical Methods*; Wiley: New York, 1988.
- [7]. Sreedhar, B., Radhika, P., Neelima, B., Hebalkar, N., Rao, M.V.B., 2009. *Polym. Adv. Technol.* 20, 950–958.
- [8]. Zhu, N., Chang, Z., He, P., Fang, Y., 2006. *Electrochim. Acta* 51, 3758–3762.
- [9]. T. Sulimenko, J. Stejskal, I. Křivka, J. Prokeš. *Eur. Polym. J.* 37, 219 (2001).