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Preparation and Characterization of Polyaniline / Glassy Carbon Modified Electrode as an Electrocatalyst for the Production of Hydrogen from $Et_3NHCl/[Bu_4N][BF_4]$-CH_3CN Solution

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Crystalline, porous and fibril-like structure polyaniline film is electrodeposited on glassy carbon electrode from acidic solution. The electrochemical behaviour of polyaniline/glassy carbon modified electrode in $[Bu_4N][BF_4]$-CH_3CN solution is investigated using cyclic voltammetry technique. It shows a stable electroactive region which is related to the semiconducting state of polyaniline in nonaqueous medium. The electro-catalytic performance of the modified electrode toward Hydrogen Evolution Reaction (*HER*) from $Et_3NHCl/[Bu_4N][BF_4]$-CH_3CN solution shows a positive shift in the direct proton reduction potential as well as a higher catalytic reduction current density compared to the unmodified electrode with a good stability of 73.7 % current retention after 25 repetitive cycles. The electrocatalytic activity of the modified electrode is correlated to its morphology.

Keywords: polyaniline, Hydrogen Evolution Reaction, electrocatalysis, cyclic voltammetry, surface characterization

1. INTRODUCTION

Hydrogen Evolution Reaction (*HER*) is considered as one of the suitable alternative sources of energy compared to fossil fuels [1,2] as it is derived from non-fossil sources, burns cleanly with no pollutants being emitted as well as it is suitable to use in a fuel cell to generate electricity [3,4]. Electrocatalytic reduction of protons has unique advantages, including that the electrolysis system can act as energy vector and energy storage medium [5]. Platinum is an ideal electrocatalyst for the electrochemical reduction of protons. However, it is an expensive metal which needs to be replaced.

Therefore, the search of new and alternative electrocatalyst materials for *HER* is of great interest for researchers [6-9]. Carbon based electrodes are important materials for electrochemical catalysis, particularly for *HER* from aqueous and non aqueous media. Furthermore, the electrocatalytic activity of these electrodes increases with their modification by electrochemically active species [10].

Conducting polymers have been used as active electrode materials for electrochemical applications because of their high charge density, fast charge/discharge kinetics and low cost [11]. Modification of inert electrodes with conducting polymers enhances the kinetics of the electrode processes as a result of the synergistic effect of their pores and active surface with the presence of free function groups which simplify the adsorption of compounds to be reduced or oxidized. Polyaniline and its derivatives are considered as one of the most studied electroactive conducting polymers, because they are easily formed as an environmentally stable film onto electrode surfaces [12].

Aydm and Koleli [13] studied the *HER* on platinum electrode in the absence and presence of polyaniline, polypyrrole and polyaniline/pyrrole copolymer films in sulphuric acid solutions. Data revealed that, the *HER* obeys Volmer-Tafel mechanism in which Tafel reaction is the rate determining step. The electrochemical response of a polyaniline/Pt modified electrode toward dissolved hydroquinone and Fe^{2+} was examined. [14]. Data clarified that, the rate of the electron self-exchange between the redox-active sites within the polyaniline film for hydroquinone was much faster than that of Fe^{2+} and the hydroquinone was strongly partitioned from the aqueous solution into the film. The electrocatalytic activity of electrodeposited polyaniline (PAni) film on platinum electrode, toward hydroquinone/ benzoquinone (HQ/BQ) and $Fe^{2+/3+}$ reactions was investigated [15]. Authors observed that, *PAni* layer assumes the behaviour of a redox polymer and the redox reactions were taking place at a polyaniline/solution interface within the *PAni* layer, but the depth of penetration of solute into the polyaniline layer depends on the diffusion coefficient of the solute through the *PAni* layer.

Electrocatalytic oxidation of formaldehyde and methanol was studied on polyaniline/platinum microelectrodes using cyclic voltammetry and chronoamperometry techniques [16]. Data showed highly electrocatalytic activity and stability of the microelectrodes toward formaldehyde and methanol electro-oxidation. Alenezi [17] reported that, the reduction potential of hydrogen evolution reaction on vitrous carbon electrode was shifted about 300 mV vs Ag/AgCl to more positive value in the presence of Fe(PFTPP)Cl as an electrocatalyst with a current efficiency of *ca.* 58% after 3.8 h in non aqueous medium.

The aim of the present work is to prepare and characterize polyaniline/ glassy carbon modified electrode from acidic solution using cyclic voltammetry technique, as well as investigating the electrochemical activity and stability of the modified electrode as an electrocatalyst toward the electro-reduction of protons from $Et_3NHCl/[Bu_4N][BF_4]-CH_3CN$ solution.

2. EXPERIMENTAL

2.1. Materials

Aniline, sulphuric acid, acetonitrile (CH_3CN), acetone, triethylamine hydrochloride (Et_3NHCl), tetrabutylammonium tetraflouroborate ($[Bu_4N]$ $[BF_4]$) are obtained from Merck Chemical Co. (Germany), and a glassy carbon working electrode is supplied from BAS Inc. (Japan). Prior to each experiment, the working electrode is polished to mirror surface with 1μm polishing diamond and 0.05 μm polishing alumina (BAS Inc. Japan), rinsed with acetone and finally washed with deionized water (18.2 μs) and dried. All experiments are carried out under inert nitrogen atmosphere.

2.2. Electrochemical Measurements:

Electrochemical measurements are performed using standard three-compartment glass cell with the glassy carbon working electrode, Pt counter electrode and Ag/AgCl reference electrode. All electrochemical experiments are performed using the Potentiostat / Galvanostat (AUTOLAB PGSTAT 128N) and NOVA 1.10 software is used for recording and fitting the obtained data.

2.3. Morphological and Spectroscopic Characterizations:

SEM analysis for as-deposited polyaniline film was carried out using JSM-6510LA (JEOL, Tokyo, Japan). The X-ray diffractometer (Philips 1976, model 1390) was operated for the polymer film adhered on the glassy carbon electrode under the following conditions, which were kept constant for all of the analysis processes: Cu X-ray tube, scan speed = 8 °/min, current = 30 mA, voltage = 40 kV, and preset time = 10 s.

Infrared measurements for aniline monomer and its polymer film were carried out using a shimadzu FTIR- 430 Jasco spectrophotometer. Ultraviolet / visible absorption spectra of aniline monomer and its polymer samples are measured using Shimadzu UV spectro-photometer (M160 PC), at room temperature in the range 200-400 nm region using chloroform as a solvent and reference.

3. RESULTS AND DISCUSSION

3.1. Preparation of polyaniline/glassy carbon modified electrode (GC/PAni):

Modification of glassy carbon electrode with polyaniline film is carried out through the electropolymerization of aniline on the glassy carbon surface from acidic solution containing 1.0 M sulphouric acid and 0.05 M aniline using cyclic voltammetry technique in the potential between 200 and 1000 mV (vs. Ag/AgCl) with a scan rate of 100 mV.s^{-1} at room temperature as shown in Figure (1). Data clearly shows three redox couples (A/A*,B/B*&C/C*) relevant to the electrodeposition of polyaniline (*PAni*) film on glassy carbon (*GC*) substrate. The first redox couple (A/A*) corresponds to the transformation of leuco-emeraldine (LM) state to the emeraldine (EM) and the third redox couple (C/C*) is attributed to the conversion of emeraldine (EM) to pernigraniline (PE) while the intermediate redox couple (B/B*) is related to the redox reaction of p-benzoquinone intermediate [12,15,18-20] as shown in Scheme (1).

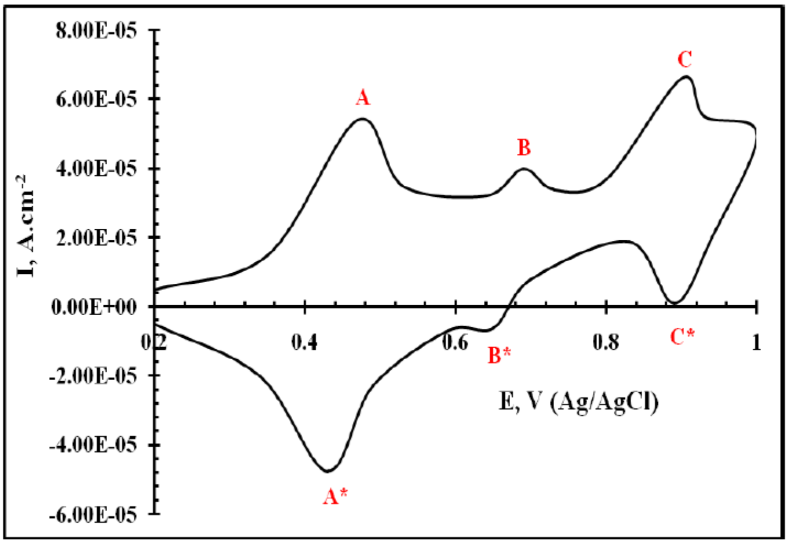
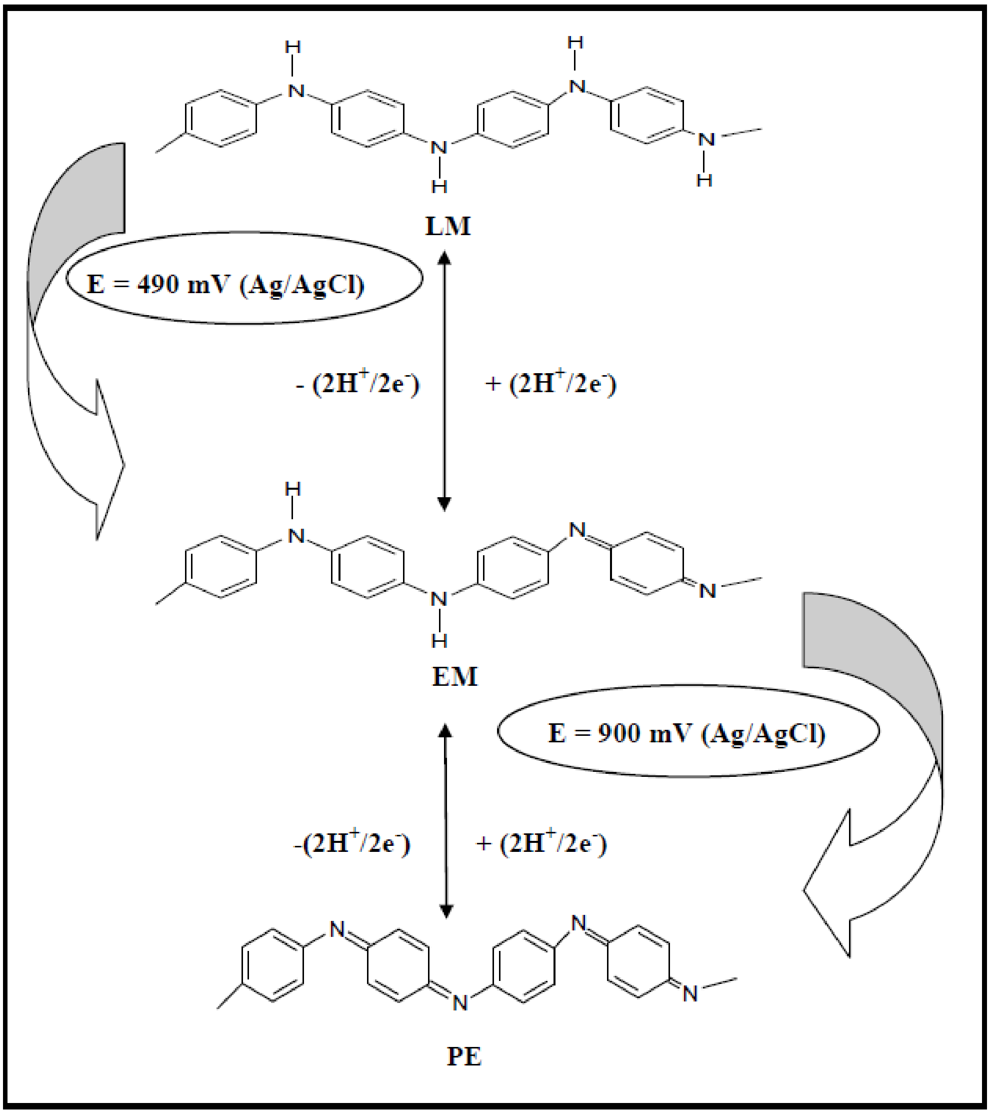


Figure 1. Cyclic voltammogram of *GC* electrode in aqueous solution containing 1.0M H_2SO_4 and 0.05M *Ani* with scan rate of 100 mV.s^{-1} at room temperature



Scheme 1. Schematic representation for the electrodeposition of *PAni* on *GC* electrode

3.2. Morphological and spectroscopic characterizations of GC/PAni modified electrode:

Homogenous, smooth, and well-adhering *PAni* film is electrodeposited on *GC* surface. The surface morphology of the as-deposited *GC/PAni* modified electrodes shows crystalline, porous and fibril-like structure film with two characteristic peaks in the range of 2θ angle between 15 and 25° for the crystalline organic polymers [21] as shown in Figure (2).

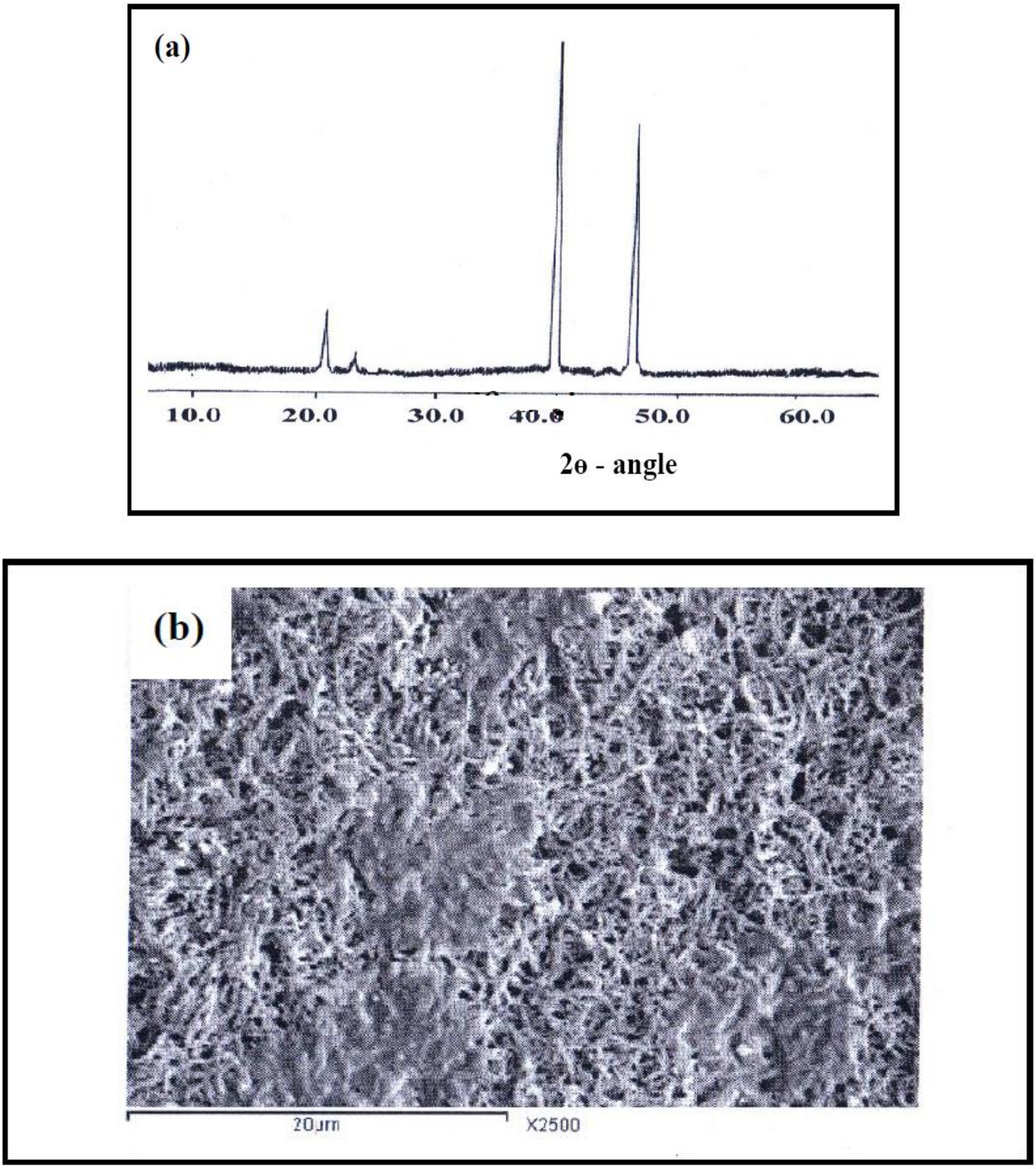


Figure 2. XRD pattern (a) and scanning electron micrograph (b) for as-deposited *PAni* film GC electrode

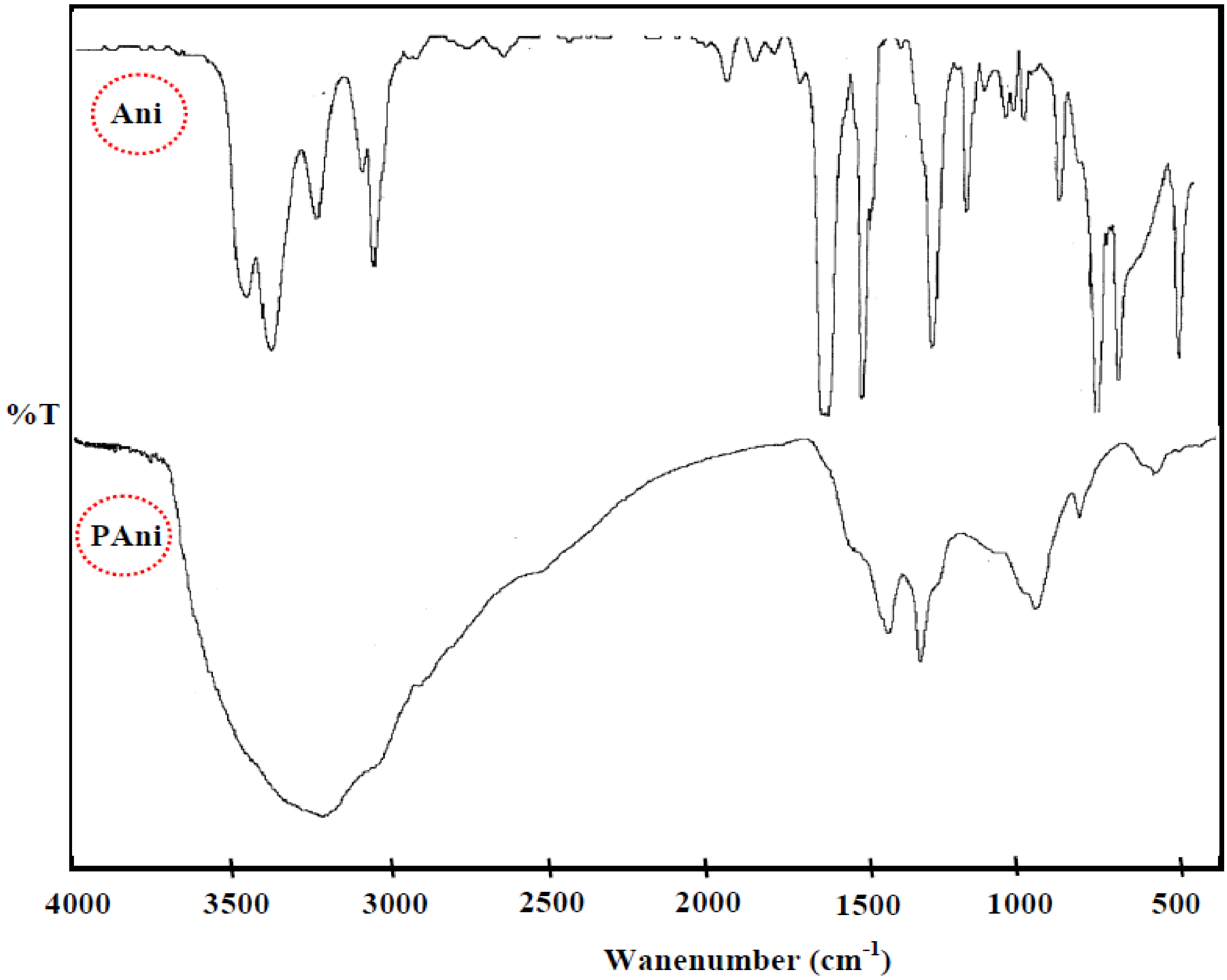


Figure 3. FTIR Spectra of *Ani* monomer and as-deposited *PAni* film

Figure (3) represents the infrared spectra for *Ani* monomer and the as-deposited *PAni* film on *GC* electrode. From the figure we can conclude that, a strong absorption band appearing at 691 cm^{-1} in case of *Ani* appears as a weak band at 690 cm^{-1} in case of *PAni* can be attributed to wagging deformation of NH_2. Three weak absorption bands appearing at 1026 ,1053 and 1118 cm^{-1} in case of *Ani*, appear as two bands at 1047 and 1174 cm^{-1} could be referred to CH- in-plane deformation. The week absorption band appearing at 1610 cm^{-1} in case of *Ani* is due to C=N stretching vibration in quinoide structure which does not exist in case of *Ani*. The medium absorption bands appear between 3213 and 3432 cm^{-1} in case of *Ani* is due to NH stretching vibrations while appearing as a broad band in the case of *PAni* due to electronic transition from the valence band to the conduction band [22-24].

UV-Visible spectra of *Ani* monomer and the as-deposited *PAni* film shows that, the presence of three absorption bands observed at λ_{max} = 246, 283 and 302 nm in case of *Ani* monomer and at λ_{max} = 201 , 223 and 231 nm in case of *PAni*. These absorption bands are attributed to the $\sigma - \sigma^*$, $\pi - \pi^*$ and $n - \pi^*$ transition. In addition, we observe a bathochromic shift at λ_{max} = 373 nm in case of *PAni* only due to the high conjugation of the aromatic polymeric chains [24].

3.3. Electrochemical activity of GC/PAni modified electrode:

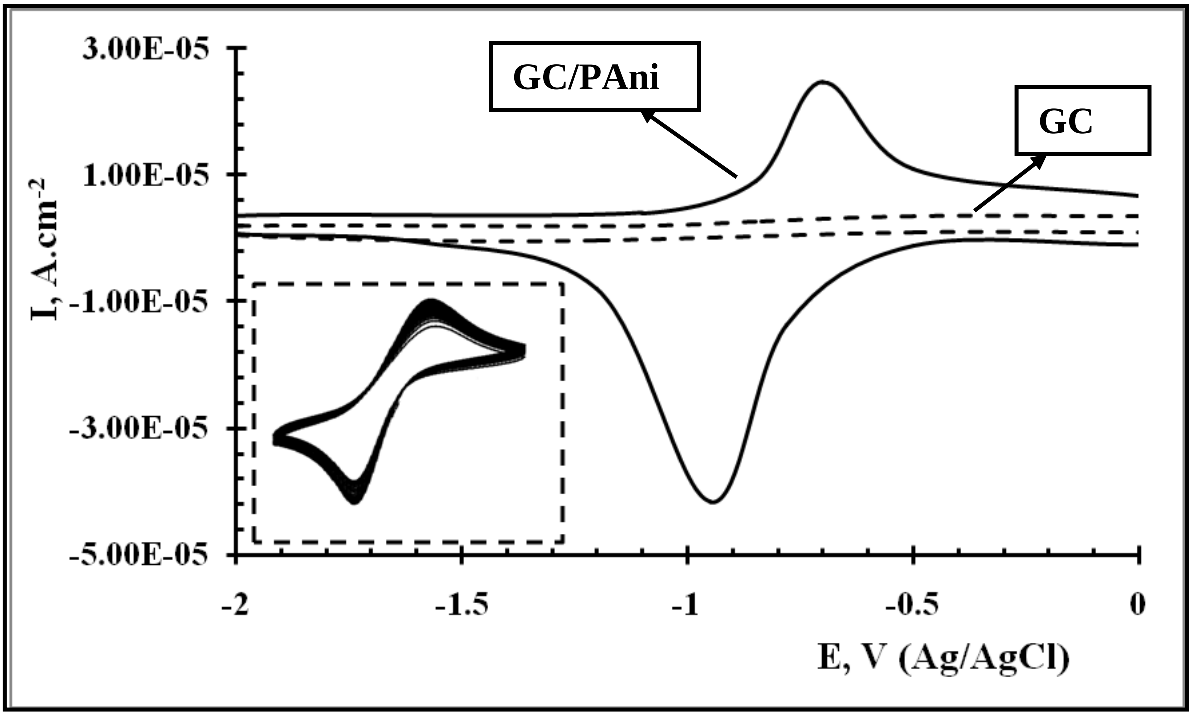
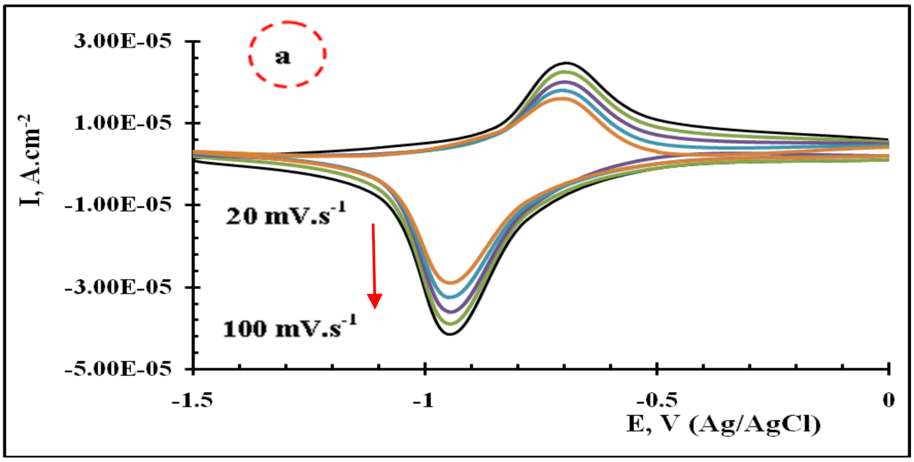


Figure 4. Cyclic voltammograms of *GC* and *GC/PAni* electrodes in 0.2 M [Bu_4N][BF_4]-CH_3CN solution at room temperature with scan rate of 100 mV. s^{-1}, the inset shows 25 repetitive cycles.

The electrochemical activity of *GC/PAni* modified electrode is studied in 0.2 M [Bu_4N][BF_4]-CH_3CN solution using cyclic voltammetry measurements in the potential range between 0.00 and -2000 mV (vs. Ag/AgCl) at room temperature, and the data are represented in Figure (4). Data illustrates that the voltammogram of *GC* electrode does not show any characteristic electrochemical response within the applied potentials, while one redox couples corresponding to the semiconducting state of *PAni* film in nonaqueous media [25] is appeared reflecting the presence of electroactive region in *PAni* film that can be used as an electractive center for the electrocatalytic applications. Stable voltammogram of *GC/PAni* modified electrode in 0.2 M [Bu_4N][BF_4]-CH_3CN solution is observed during the progressive polarization up to 25th repetitive cycles as shown in the inset of Figure (4).



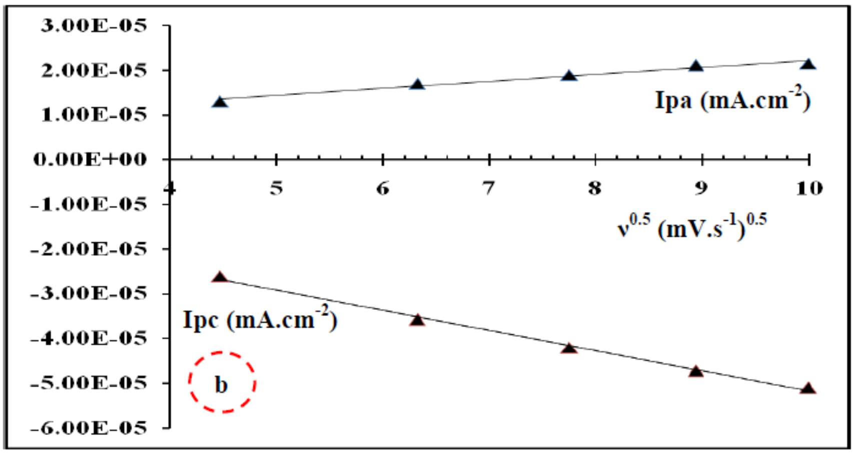


Figure 5. (a) Cyclic voltammograms of *GC/PAni* electrode in 0.2 M [Bu_4N][BF_4]-CH_3CN solution at room temperature with different scan rate, (b) Relation between $v^{0.5}$ and current (anodic and cathodic) densities

Figure (5) represents the influence of the scan rate on the voltammograms of *GC/PAni* modified electrode in 0.2 M [Bu_4N][BF_4]-CH_3CN solution in the potential range between 0.00 to -1500 mV (vs. Ag/AgCl) at room temperature. It is clear that, the anodic and cathodic current densities of the redox peaks increase with increasing the scan rate and the linear dependence between the current densities and the square root of the scan rate (20 to 100 mV.s^{-1}) refers to the electrochemical activity of the surface redox couple [26, 27].

3.4. Electrocatalytic production of hydrogen:

Electro-reduction of Et_3NHCl on *GC* and *GC/PAni* modified electrodes from 0.2 M [Bu_4N][BF_4]-CH_3CN solution is studied using cyclic voltammetry technique in the potential range between 0.00 to -2000 mV (vs. Ag/AgCl) with a scan rate of 100 mV.s^{-1} at room temperature and the data are graphically represented in Figure (6).

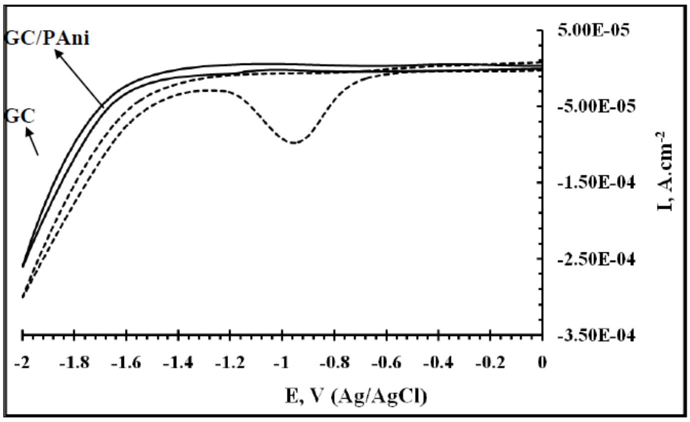


Figure 6. Cyclic voltammograms of *GC* and *GC/PAni* electrodes in 0.2 M [Bu_4N][BF_4]-CH_3CN solution containing 0.05 M Et_3NHCl at room temperature with scan rate of 100 mV.s^{-1}

Data shows that, there is one reduction peak for the *HER* which appears at -1600 mV (vs. Ag/AgCl) in case of *GC* electrode compared with two reduction peaks at -950 and -1500 mV (Ag/AgCl) for *GC/PAni* modified electrode. The first reduction peak for the modified electrode corresponds to the semiconducting state of *PAni* film [25] while the second peak refers to the *HER*. The appearance of the *HER* at more negative potential (-1500 mV) relative to the reduction of *PAni* film (-950 mV) suggests that the *PAni* film acts as an efficient electrocatalyst for the *HER*. This finding is in agreement with the positive shift (160 mV) in the potential of the *HER* and the higher redution current density in case of *GC/PAni* compared to *GC* electrodes. The electrocatalytic performance of the *GC/PAni* modified electrode can be related to its crystalline, porous and fibril-like structure, which is an important factor for the using of the conducting polymers as an electrocatalytic materials [28]. The porous and fibril-like structure of *GC/PAni* modified electrode increases its interfacial electroactive sites and enhances the penetration process through the electrode / electrolyte interface leads to increasing the charge transfere kinetics [29].

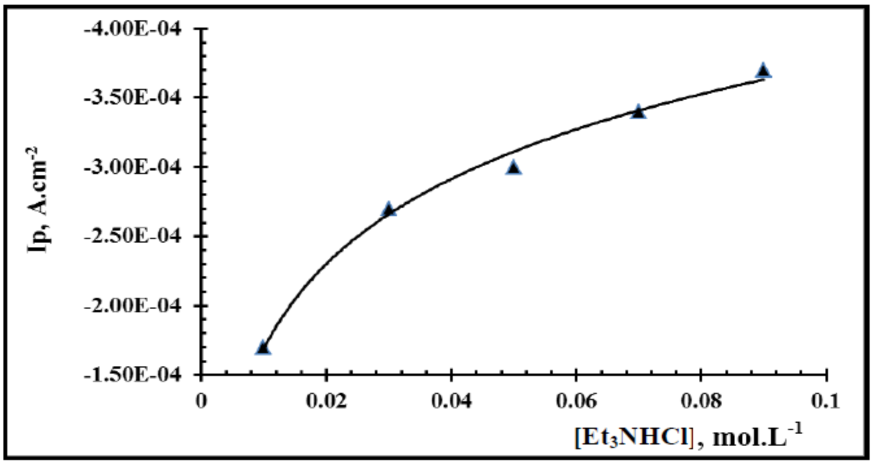


Figure 7. Cathodic peak current densities (Ipc) of *HER* versus acid concentrations

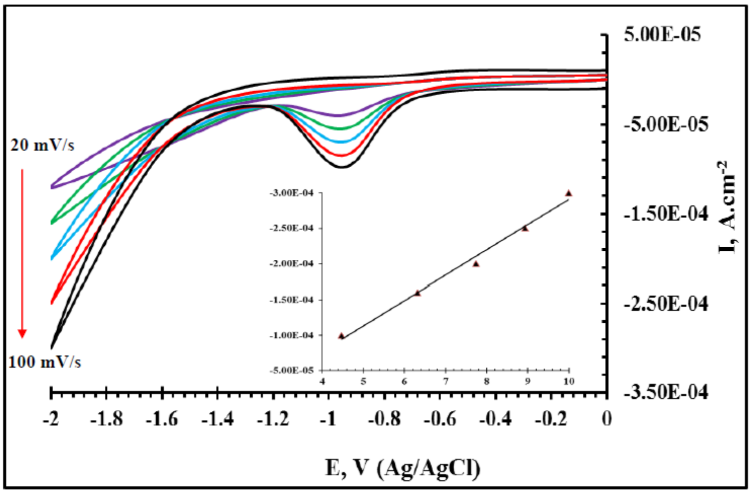


Figure 8. Cyclic voltammograms of *GC/PAni* electrode in 0.2M [Bu_4N][BF_4]-CH_3CN solution containing 0.05M Et_3NHCl at room temperature with different scan rate, the inset relation between $\nu^{0.5}$ and the cathodic current densities

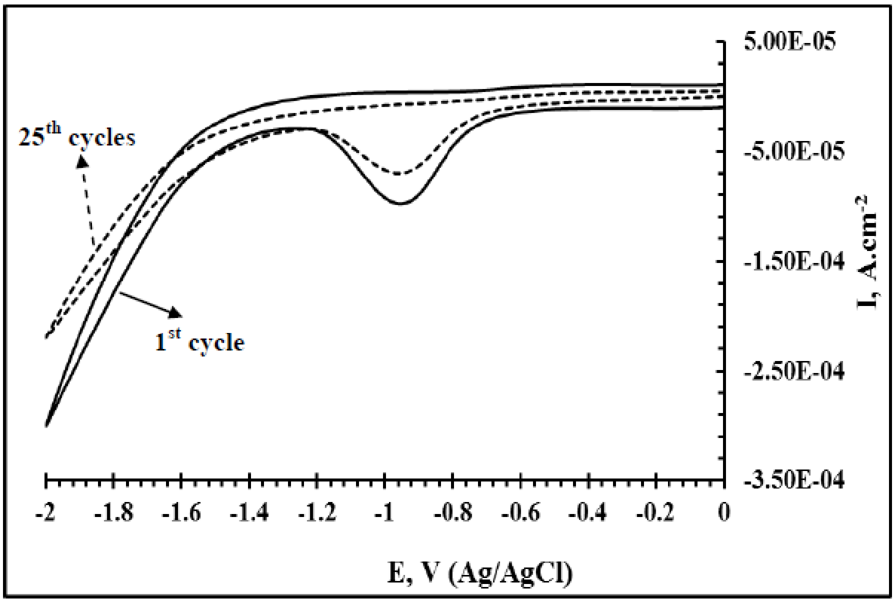


Figure 9. Repetitive 25th cycling test of *GC/PAni* electrodes in 0.2 M [Bu_4N][BF_4]-CH_3CN solution containing 0.05 M Et_3NHCl at room temperature with scan rate of 100 mV.s^{-1}

The effect of Et_3NHCl concentrations from 0.01 to 0.09 M (> 0.1 M the solubility of acid is limited in CH_3CN) on the cathodic peak current densities (Ipc) of the *HER* is studied. Figure (7) illustrates the increasing of Ipc with the acid concentrations as a result of increasing the amount of adsorbed protons on the active surface area of *PAni* which is agrees with a previously published work on the benzyl alcohol electro-oxidation [24]. Figure (8) shows the voltammograms for *GC/PAni* modified electrode with different scan rates (20 – 100 mV.s^{-1}) in 0.2M [Bu_4N][BF_4]-CH_3CN solution containing 0.05 M Et_3NHCl. Figure state that, the cathodic peak current densities of both the *HER* and the active center of *PAni* increase with increasing the scan rate as well as there is a linear dependence of the cathodic current densities with the square root of the scan rate (inset for Figure 8), these results indicate that the *HER* is kinetically a diffusion controlled process[24,30].

The short term stability is an important factor to evaluate the electrocatalytic performance of the *GC/PANi* modified electrode. Figure (9) shows the repetitive 25 cycling test at a scan rate of 100 mV.s^{-1} , the catalytic cathodic current density (-1.9x10^{-4} A.cm^{-2}) performs 73.7% retention after 25 cycles, the decrease in the catalytic current density can be explained as a result of the decreasing in proton concentrations resulting from the continuous reduction of Et_3NHCl on the modified electrode.

4. CONCLUSION

1- GC/PAni modified electrode is prepared by the electropolymerization of aniline monomer on glassy carbon surface from acidic solution.

2- Morphology of the GC/PAni modified electrode shows crystalline and porous, fibril-like structure film.

3- GC/PAni modified electrode shows a stable electroactive region in $[Bu_4N][BF_4]$-CH_3CN solution related to the semiconducting state of PAni film.

4- GC/PAni modified electrode acts as an efficient electrocatalyst for the HER with 160 mV shift in the positive direction compared to GC electrode.

5- GC/PAni modified electrode gives a catalytic current density of -1.9 x 10^{-4} A.cm^{-2} with a good stability of 73.7 % current retention after 25 repetitive cycles.

6- The electrocatalytic activity of the GC/PAni modified electrode is correlated to its crystalline, porous and fibril-like structure.

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References

1. J. A. Turner , *Science*, 285(1999)687.
2. Y. Liu, J. Li, F. Li, W. Li, H. Yang, X. Zhang, Y. Liu and J. Ma, *J. Mater. Chem. A*, 4(2016)4472.
3. S. J. Xu, D. Li and P. Y. Wu, *Adv Funct. Mater.*, 25(2015)1127.
4. Y. Liang, Q. Liu, Y. Luo, X. Suna, Y. He and A. Asiri, *Electrochim Acta*, 190(2016)360.
5. K. Xiong, L. Li, Z. Deng, M. Xia, S. Chen, S. Tan, X. Peng, C. Duan and Z. Wei, *RSC Adv.*, 4(2014)20521.
6. M. Torabi and A. Dolati, *J. Appl. Electrochem.*, 40(2010)1941.
7. J-B. Raoof, S. Hosseini and S. Mousavi-Sani, *Chinese J. Catal.*, 36(2015)2016.
8. L. Sun, D. Ca and J. Cox, *J. Solid State Electr.*, 9(2005)816.
9. Y. Zheng, Y. Jiao, Y. Zhu, L. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec and S. Qiao, *Nat. Commun.*, 5(2014)3783.
10. N. Pocard, D. Alsmeyer, R. McCreery, T. Neenan and M. Callstrom, *J. Mater. Chem.*, 2(1992) 771.
11. B. Garcia, F. Fusaiba and D. Belanger, *Can. J. Chem.*, 75(1997)1536.
12. G. Fomo, T. Waryo, P. Baker and E. Iwuoha, *Int. J. Electrochem. Sci.*, 11(2016)10347.
13. R. Aydm and F. Koleli, *Prog. Org. Coat.*, 56(2006)76.
14. J. Yano, K. Ogura, A. Kitani and K. Sasaki, Synth. Met., 52(1992)21.
15. Z. Mandić and L. Duić, *J. Electroanal. Chem.*, 403(1996)133.
16. R. Yan and B. Jin, *Electrochim. Acta*, 115 (2014) 449.
17. K. Alenezi, *Int. J. Electrochem. Sci.*, 12 (2017) 812
18. A. Eftekhari, *Synth. Met.*,145(2004)211.
19. K. Darowicki and J. Kawula, *Electrochim. Acta*, 49(2004)4829.
20. Y. Wang and K. Levon, *Macromol. Symp.*, 317(2012)240.
21. S. M. Sayyah, S. S. Abd EL Rehim and M. M. EL- Deeb, *Inter. J. Polymeric Mater.*, 53(2004)941.
22. R. M. Silverstein, C. G. Bassler and T. C. Morill, *Spectroscopic identification of organic compounds*, Wiley: New York, 1974.
23. S. M. Sayyah, S. S. Abd El-Rehim and M. M. El-Deeb, *J. Appl. Polym. Sci.*, 94 (2004)941.
24. M. M. EL-Deeb and H. Al-Shamari, *Int. J. Electrochem. Sci.*, 11 (2016) 8447.
25. F. Fusalba, P. Gouérec, D. Villers and D.Bélanger, *J. Electrochem. Soc.*, 148(2001)A1.
26. A. J. Bard and L. R. Faulkner, *Electrochemical methods*, New York: Wiley; 2001. p. 591.

27. I. Danaee, M. Jafarian, F. Forouzandeh, F. Gobal and M.G. Mahjani, *Int. J. Hydrogen Energ*., 33 (2008) 4367.
28. A. Malinauskas, *Synth. Met*., 107(1999)75.
29. R. Ding, L. Qi, M. Jia and H. Wang, *Electrochim. Acta*, 113 (2013) 290.
30. A. Shaha, N. Yasmeena, G. Rahmana and S. Bilal, *Electrochim. Acta*, 224 (2017)468.