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Electrochemical Deposition and Properties of Polyaniline Films on Carbon and Precious Metal Surfaces in Perchloric Acid/ Acetonitrile

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Beside the electrochemical polymerization of polyaniline (PANI) films on electrode surface, the medium of polymerization and the metal surfaces are essential to increase the yield and electrical conductivity of PANI formed. The electrochemical synthesis of films of PANI on pyrolitic graphite (PG), glassy carbon, gold and platinum electrodes in perchloric acid/acetonitrile solution (0.1 M $HClO_4$/ACN) was investigated. Linear scan voltammograms (LSV) for these electrodes exhibited similar onset potentials (E_{onset} = 0.89 to 0.94 V) for the oxidation of aniline into its radical cation. The heterogeneous electron transfer constants at the onset potentials ($k_{et\text{-}onset}$) varied as follows: Pt (7×10^{-8} cm s^{-1}) ≈ GC> Au > PG (0.6×10^{-8} cm s^{-1}). During multi-cyclic potentiodynamic electropolymerization processes, three pairs of anodic and two pairs of cathodic growth-peaks were observed for Pt, GC, Au, but three pairs cathodic growth-peak for PG. All electrodes present good stability vis-a-vis PANI. Outcomes of further studies on the resulting films, carried out with cyclic voltammetry (CV) are discussed and the resultant PANI thin films can be used as transducer in the construction of sensors platform.

Keywords: Polyaniline, organic medium, pyrolytic graphite electrode, gold electrode

1. INTRODUCTION

Pristine polyaniline (PANI) is a special kind of conducting electroactive organic polymer which shows many interesting properties such as electrochemical redox behavior, electrochromic [1] catalytic activities [2-4]. Polyaniline being environmental stable, the conductivity easily controllable, many researchers reported on this conducting polymer by interesting on the redox properties associated with the chain nitrogen atoms [5]. Polyaniline also economically continues to be attractive despite the discovery of numerous polyaniline derivatives based on functionalized aniline [6-7]. The properties and several applications of PANI obtained depend on synthesis parameters such as the technique of electrosynthesis and the composition of the polymerization solution. Of particular interest is the electropolymerization of this most readily available monomer into conductive PANI films.

Electrochemical polymerization also called electropolymerisation using for this study is a typical method generally used for the synthesis of PANI coating [8] because of its simplicity and reproducibility. In general, this method consists of applying a potential to a working electrode immersed in electrochemical cell containing an electrolyte solution with the reference and counter electrodes. The monomer is thus electrochemically oxidized given place to the polymerization to occur at the electrode surface with deposition of the polymer film. The first step of the synthesis is the formation of $C_6H_5\text{-}NH_2^+$ cation radical via the transfer of an electron from a sp^3 orbital of nitrogen atom to the electrode when oxidation occurred. During polymerization, the PANI chain propagation starts with the formation of non-conducting PANI, leucoemeraldine (oxidation state $n = 1$) complete reduction state and terminates with the formation of the most conductive PANI form, the emeraldine ($n = 0.5$) oxidation state. In some cases, when using this method, the intermediate process occurs, and it forms the pernigraniline ($n = 0$) fully oxidized state [9]. This technique presents as advantages greater simplicity and reproducibility, completed coverage of the active surface, greater control over film thickness and perhaps provide a means for the entrapment of both the specific agent and a suitable mediator. Moreover, electropolymerisation is a cheap technique and polymerization media can be used repeatedly. For electrochemical methods, potentiostatic, galvanostatic and potential sweep methods are usually used for electropolymerisation of PANI and its derivatives. The commonly used working electrodes are conducting substrates such as gold, carbon, platinum and indium-tin oxide coated glass plates [10].

On the other hand, the low cost of the monomer and its easy synthesis in different aqueous medium confer to polyanilines more advantages. The synthesis of PANI is performed generally in aqueous acid solutions [11] and neutral aqueous media [12], either chemically or electrochemically. But in the case of organic media, it was considered that good quality of PANI films cannot be obtained. Indeed, in aqueous acids, some acids such as hydrochloric acid, sulfuric acid [13], oxalic acid and nitric acid [14-16], oxalic acid [8] have been used; In aquous salts, copper (II) nitrate, sodium sulfate, sodium sulfate/sodium perchlorate, lithium perchlorate, sodium benzoate, and propylene carbonate/lithium perchlorate [17-24] have been used; In organic acid electrolytes, many electrolyte solution as tetramethylammonium trifluoromethane-sulfonate/acetonitrile, periodic acid/tetraethylammonium tetrafluoroborate/acetonitrile, trichloromethan, tetrabutylammonium tetrafluoroborate /trifluoroacetic acid, tetrabuthylammonium perchlorate/acetonitrile and perchloric acid/benzenesulfonic acids [25-27] have been used in the electrosynthesis of PANI; In ionic liquids electrolytes the ionic solution such as 1-methyl-3-butylimidazolium tetrafluoroborate [28-32] has been investigated; In addition, PANI has been electrosynthesized in fluoride medium such as ammonium fluoride and hydrofluoric Acid [33]. From these previous studies done on the synthesis of polyaniline in different media, some of them have shown that the medium of the polymerization affects the properties of the polyaniline. For example, the yield and electrical conductivity of emeraldine salt-form PANI prepared in acid medium is increased by decreasing the ionic strength of the acid [34].

Not all possible combinations of electrolytes and solvents have been investigated in the list above. In this work we report the first electropolymerization of aniline in $HClO_4$/ACN, comparatively presenting its electro-oxidation as well as growth rates and electroactivities of the resulting PANI films on four types of electrodes. On the other hand, this research study intends to prove that PANI does not deteriorate on scanning and will therefore find applications in electrochemical sensor [35].

2. EXPERIMENTAL SECTION

2.1. Reagents.

Aniline ($C_6H_5NH_2$, 99%) from Sigma-Aldrich South Africa, Aston Manor, Johannesburg, South Africa, was purified by distillation under vacuum and the resulting pure stock aniline was stored at (-) 20 °C. Perchloric acid ($HClO_4$, 70%) and acetonitrile (ACN, 99.8%) anhydrous, were also procured from Sigma-Aldrich Company. Ethanol (C_2H_6O, 99.9%) absolute was purchased from Kimix Chemical Company, Cape Town, South Africa.

2.2. Preparation of electrodes and materials

A conventional three-electrode cell was used. The working electrodes were the glassy carbon (GC) (diameter of 3 mm), platinum (Pt) (diameter of 1.6 mm), gold (Au) (diameter of 1.6 mm) were obtained from Bioanalytical Systems (BAS) and pyrrolytic graphite (PG) (diameter of 3 mm) electrode was purchased from AMEL Electrochemistry (Milano, Italy). Electrodes preparation involved successive polishing of working electrode with fine grades of alumina slurries of 1.0, 0.3 and 0.05 μm from Buehler Micropolish (Lake Bluff, IL, USA) respectively, washing with distilled water after each step of polishing and sonicating for 5 minutes in distilled water and then in ethanol successively. A silver wire (pseudo-reference electrode) was used as reference electrode to avoid water in the polymerization medium and a platinum wire as auxiliary electrode. Electrochemical experiments were carried out using a MOD-7050 potentiostat, AMEL Electrochemistry, Milano, Italy, connected to a personal computer through a USB electrochemical interface. All measurements were made at 25 ^{o}C.

2.3. Electrosynthesis of PANI

This experiment was performed in organic solution of 5 mL ACN containing 0.05 M aniline in presence of 0.1 M $HClO_4$. The oxidation of aniline was carried out by recording the linear scan voltammograms (LSVs) of aniline on GC, Pt, PG and Au electrodes at different potential range of (-) 0.2 and +2 V for Pt, (-) 0.5 and +2.5 V for PG, (-) 0.3 and +2.5 V for Au, (-) 0.5 and +1.8 V for GC electrode. The purpose of this experiment was to determine the onset potential which was further used for electrosynthesis. Electrochemical polymerization of aniline on the bare GC, Pt, PG, Au electrodes was performed by a potentiodynamic method with a scan rate (ν) of 50 mV s^{-1} between - 0.1 to 1.47 V for Au, 0.1 to 1.3 V for GC and PG, and 0.0 to 1.3 V for Pt in the electrolyte solution of 0.1 M

$HClO_4$/ACN containing 0.05 M of aniline. For electrochemical characterization purpose of the PANI deposited electrodes, the PANI film was produced over 15 cycles and the electrodes were rinsed with ethanol prior to their study.

2.4. Study of PANI films and reversibility of the system

The experiment on the electrochemical reversibility of the system was studied by recording the cyclic voltammograms of PANI in the electrosynthesis potential range of each electrode at 50 mV s^{-1} in 0.1 M $HClO_4$/ACN. The CVs were recorded for three multiple cycles under controlled potential, in the respective electrosynthesis range of each electrode versus silver wire reference electrode. The CVs of the modified-PANI films were recorded in 0.1 M $HClO_4$/ACN at scan rates of 15, 20, 50, 75, 100, 300 mV s^{-1}.

3. RESULTS AND DISCUSSION

3.1. Electro-oxidation of aniline

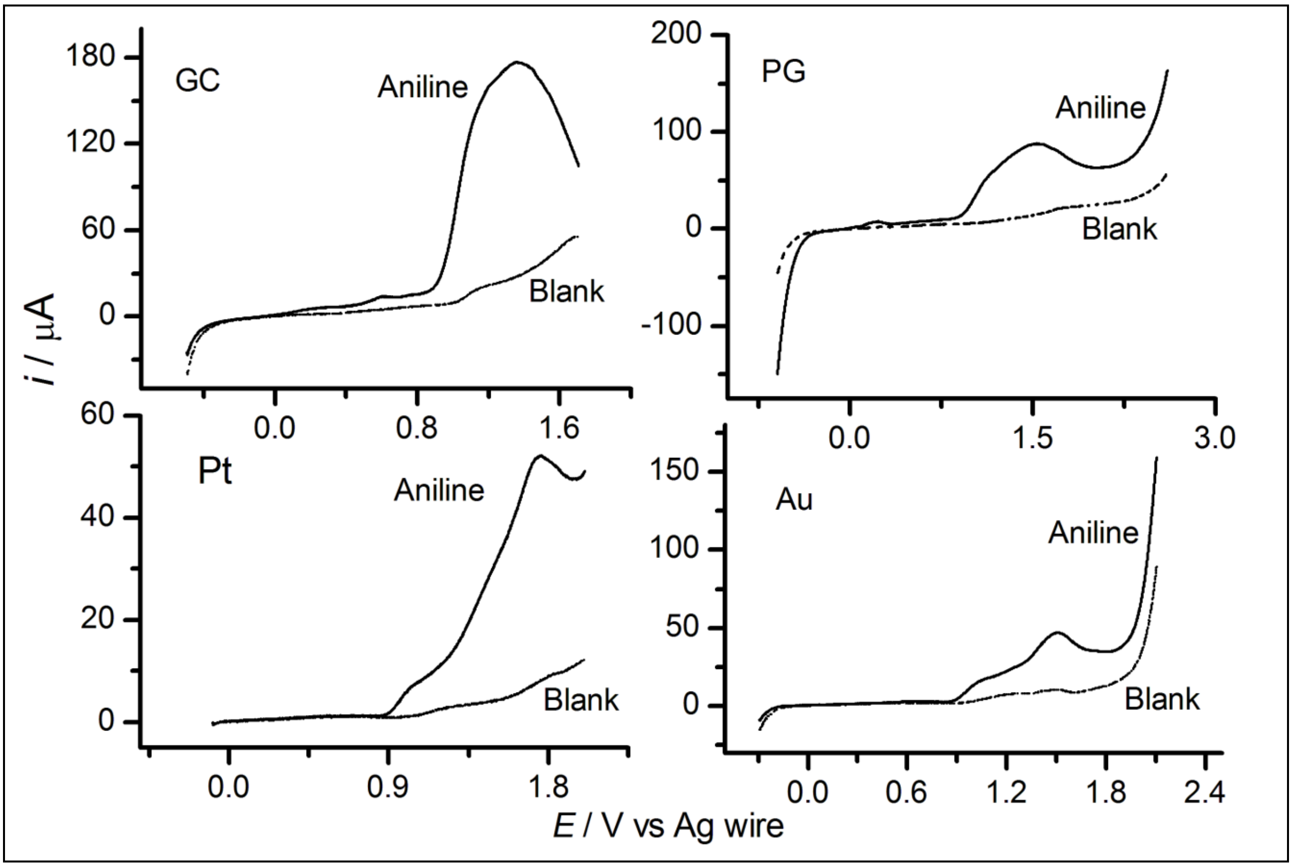


Figure 1. LSVs of electro-oxidation of aniline in 0.1 M $HClO_4$/CAN.

Linear scan voltammetry (LSV) at 50 mV s^{-1} scan rate over different potential ranges for each electrode in 0.1 M $HClO_4$/ACN was used as a standard method to oxidize aniline monomer. The linear scan voltammograms (LSVs) were recorded, Figure1, show that the aniline monomers have been oxidized and ready to be polymerized.

Two oxidation peaks, are apparent around +0.6 and +1.6 V for Pt, Au, GC and only the second one is apparent around +1.5 V for PG . The first peak has been related to the oxidation of aniline [36]. The second peak corresponds either to the oxidation of p-aminodiphenylamine to form the benzidine diffusing closes to the electrode, or to the overoxidation of aniline [37]. The onset potential (E_{onset}) which is the potential corresponding to the oxidation of aniline was determined graphically from LSVs and the value is given in Table1.To compare the different scans obtained with the different electrode systems, the current related to each electrode was determined as well as we determined the onset potential. The characteristic peak of aniline for each electrode is clearly seen in all cases. From the E_{onset}, + 0.4 V was added to find the final potential (E_2) used for the electropolymerization.

The kinetics of the oxidation of aniline was studied by measuring the open circuit voltage (E_{OCV}) of aniline at different concentration and the Figure 2 and 3 were obtained.

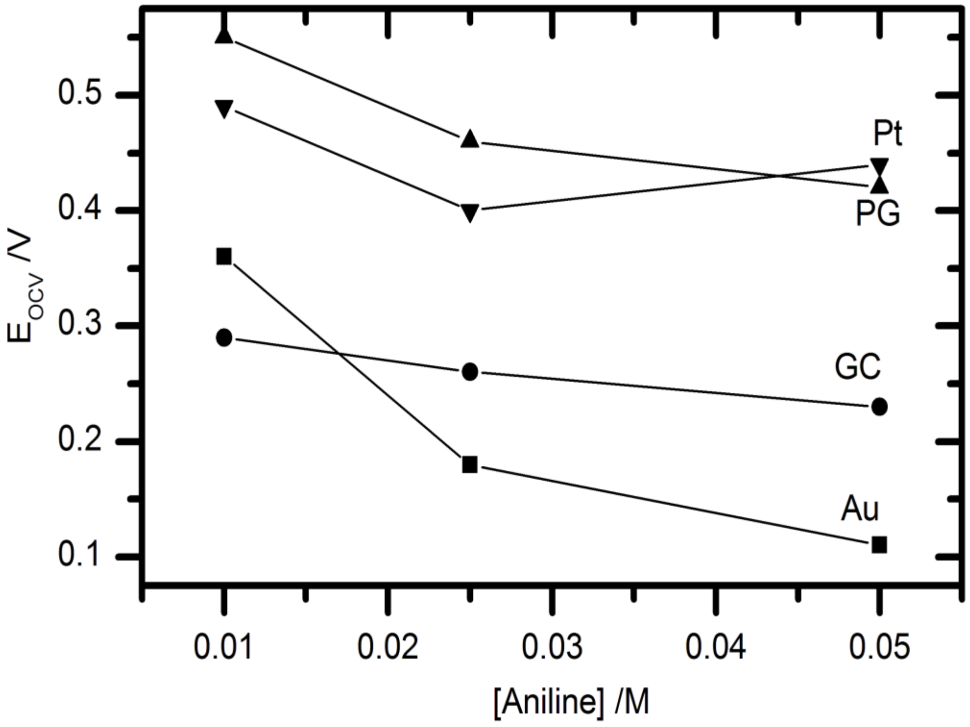


Figure 2. Plot of E_{OCV} *vs*. [Aniline]

The rate of the oxidation ($k_{\text{a-onset}}$) and the extension coefficient (α) can be determined using the equation (1)

$$i_a = i_0 e^{\frac{(1-\alpha)nF(E-E_{OCV})}{RT}} \qquad (1)$$

Where $i_0 = nFAC_R^{bulk(1-\alpha)} C_O^{bulk(\alpha)} K^0$ (2)

but because the E_{OCV} depends on the concentration of aniline (Figure 2), the slope,

$$slope = (1-\alpha)nF/2.3RT \qquad (3)$$

of Tafel plot (Figure 3) was used to determine the extension coefficient (α) with n = 1 [38].

Using equation (4), the charge transfer resistance (R_{ct}) and the exchange current (i_o) were determined.

$$R_{ct} = dE/di \leftrightarrow dE = R_{ct}di \rightarrow di/dE = 1/R_{ct} \qquad (4)$$

Form the above data and with the Butler-Volmer equation (5), the electrochemical oxidation kinetic of PANI can be exploited through Tafel slopes [18] as show in Figure 3.

$$\log|i_{net}| = \log\left(nFAk^{0}C_R^{bulk(1-\alpha)}C_O^{(\alpha)}\right) - \frac{(1-\alpha)nF}{2.3RT}(E-E_{OCV}) \qquad (5)$$

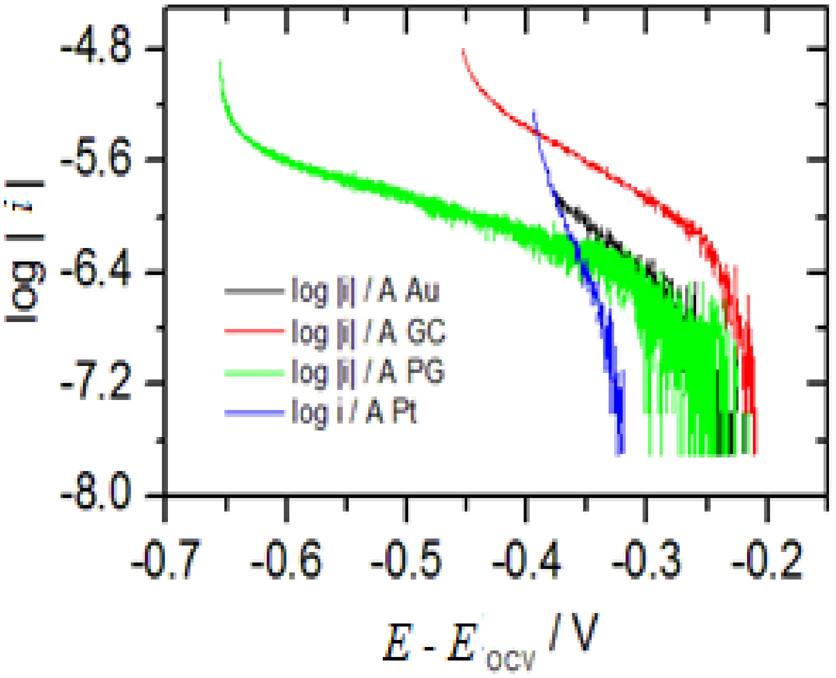


Figure 3. Tafel plot for the electro-oxidation of aniline in 0.1 M $HClO_4$/ACN.

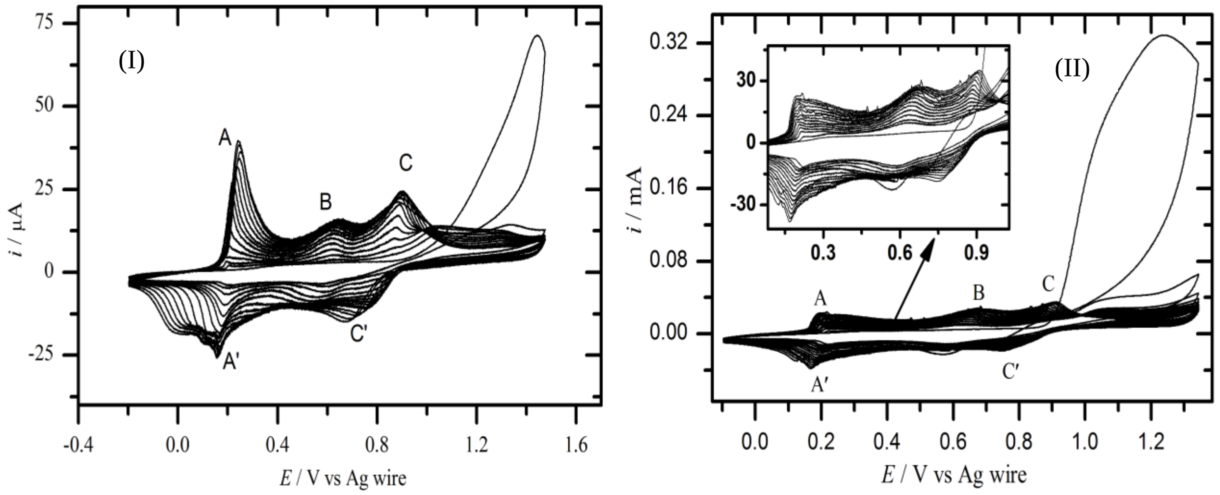
Table 1. Kinetic parameters for electro-oxidation of aniline in 0.1 M $HClO_4$/ACN.

Electrodes	Au	GC	PG	Pt
E_{onset} (V)	0.89	0.94	0.93	0.89
α_α	0.55	0.39	0.53	0.66
$k_{net\text{-}onset}$ x 10^{-8} (cm s^{-1})	2.1	6.8	0.6	6.9
i_{onset} (μA mm^{-2})	2.05	3.26	2.06	0.33

3.2. Electrochemical polymerization of aniline

The best criterion for PANI films on the electrode surface for wide applicability and, usually good performance of electrode is a method of synthesis and the medium for the synthesis. Figure4 shows the CVs recorded during the continuous scan over 15 cycles at 50 mV s^{-1} scan rates in different potential ranges and on the various electrodes in 0.1 M HClO$_4$/ACN containing 0.05 M aniline. For the first potential sweep, aniline is oxidized, resulting in an irreversible anodic current peak. The part of the product yielded from aniline oxidation is deposited on the electrode surface, which corresponds to the growth process taking place with cathodic current peak (C') appearing. The intensity of first peak current decreases and finally disappears when the number of cycles increases. The CVs show that the current increases in each successive cycle which confirms the electrodeposition of PANI films. The redox peak at about 0.40 to 0.50 V (AA') corresponds to the transformation of the reduced leucoemeraldine state to the partly oxidized emeraldine state. The redox peak around 0.70 and 1 V (CC') is attributed to the transition leucoemeraldine reduction state to pernigraniline full oxidation state. Intermediate reactions such as *p*-benzoquinone, *p*-aminophenol and some dimers reductions occur during the polymerization and these molecules are known to be trapped in the polymer [38]. The intermediate peaks (BB') is generally attributed to the redox reaction of *p*-benzoquinone [16, 39-40]. During the anodic scan, the first oxidation peaks are obtained in the initial cycle and the peak potential maintained almost the same.

Generally in electropolymerisation processes, the increase of the voltammetric peak current density and the scan number are an indication of the growth rate of polymer. The polymerization rate (V) for the cathodic peak related to the quantity of polymer is measured and plotted against scan number in Figure 4. Using the equation $V = - k_{app}$ [monomer] (cathodic peak), where k_{app} is a set of apparent-first-order reaction rate constant, V is the rate of polymerization which corresponds to the slope of the curve [41], the quantity of polymer formed on the electrode surface was determined. As shown in Figure 4, the amount of PANI deposited on PG is almost double the amount formed on GC, Pt, and Au electrodes. The apparent rate constant ($k_{\mathrm{p}}^{\mathrm{app}}$) for the polymerization step per cycle was estimated from the plot $i_{\text{pc-growth}}$ vs. cycle number. This parameter determines the kinetic of the electropolymerization.



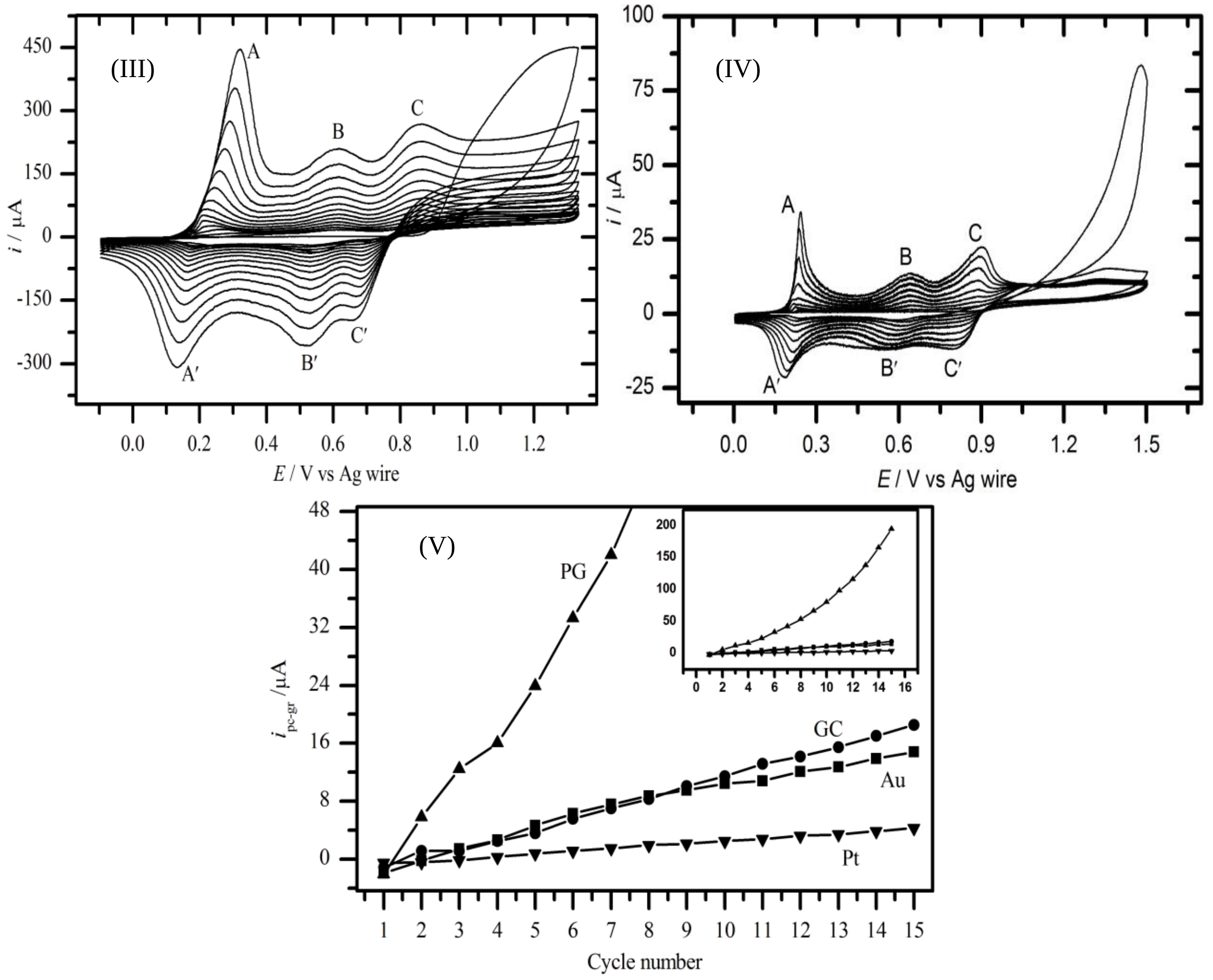


Figure 4. CVs obtained from the potentiodynamic scan of PANI films deposited on Au (I), GC (II), PG (III) and Pt (IV) electrodes in 0.1 M $HClO_4$/ACN with 0.05 M aniline at 0.05 V s^{-1}. (V) The dependence of (the growth of) the cathodic peak current of PANI on CV cycle number.

During the potentiodynamic growth of individual PANI films, the anodic current measured during each potential scan cycle was integrated to generate the anodic charge transfer density Q_a. The following values were obtained for each electrode:

Q_a(Pt) < Q_a(GC) < Q_a(Au) < Q_a(PG). This electropolymerization charge transferred at the interface between the electrode surface and the solution is proportional to the quantity of polymer formed on the electrode surface. Thus, the previous values of Q_a obtained, show that more PANI is formed on the PG electrode surface. The rates of electron transfer reaction occurred in the interface electrode surface|electrolyte is one of the most important parameter studied in electrochemistry. Similarly, the heterogenous rate electron transfer is of great use for the study of the kinetics of the reaction at the electrode Surface, whereby the electrode processes can occur through the reaction pathway which involves adsorbed intermediates [42]. For reversible or quasi-reversible reactions, the rate constants is determined by the slope of the graph $i_{pc\text{-}gr}$ *vs*. cycle number (Figure 4) was calculated and the correlation coefficient was R^2 = 0.998, 0.999, 0.997 and 0.998 on Au, GC, PG and Pt electrode respectively. That slope calculated per area of each surface of electrode was directly proportional to the apparent heterogeneous rate constant k_{app} of polymerization per cycle and it was observed that $k_{app\text{-}polym}$(Pt) < $k_{app\text{-}polym}$(GC) < $k_{app\text{-}polym}$(Au) < $k_{app\text{-}polym}$(PG). The charge transfer and polymerization rate were calculated from the first cathodic peak current which is the growth-peak ($i_{pc\text{-}gr}$) in the redox process of PANI. The above values of $k_{app\text{-}polym}$ (77.11 (Au), 20.22 (GC), 133.5 (PG) and 17.41 A cm^{-2} s^{-1} (Pt)) are related to the values of Q_a (13.65 (Au), 9.6 (GC), 35.9 (PG) and 5.15 C cm^{-2} (Pt)) which explain the amounts of PANI formed on the electrode surface during the electropolymerisation process.

3.3. Study of the PANI films in HClO$_4$/ACN

The electrochemical stability of conducting polymers is of primary interest, particularly in different fields of technology such as batteries, electrochromic devices and sensors, supercapacitors [43-44]. Their stability depends on the type of acids, which constitutes the salt with PANI [45]. Among all the conducting polymers, it is known that polyaniline and polypyrrole have good electrochemical stability [46]. The CV was used to study the stability of the electrode surface vis-à-vis PANI. The stability of the modified electrode over three repetitive scans within the potential window of each electrode in 0.1 M HClO$_4$/ACN solution should be emphasized.

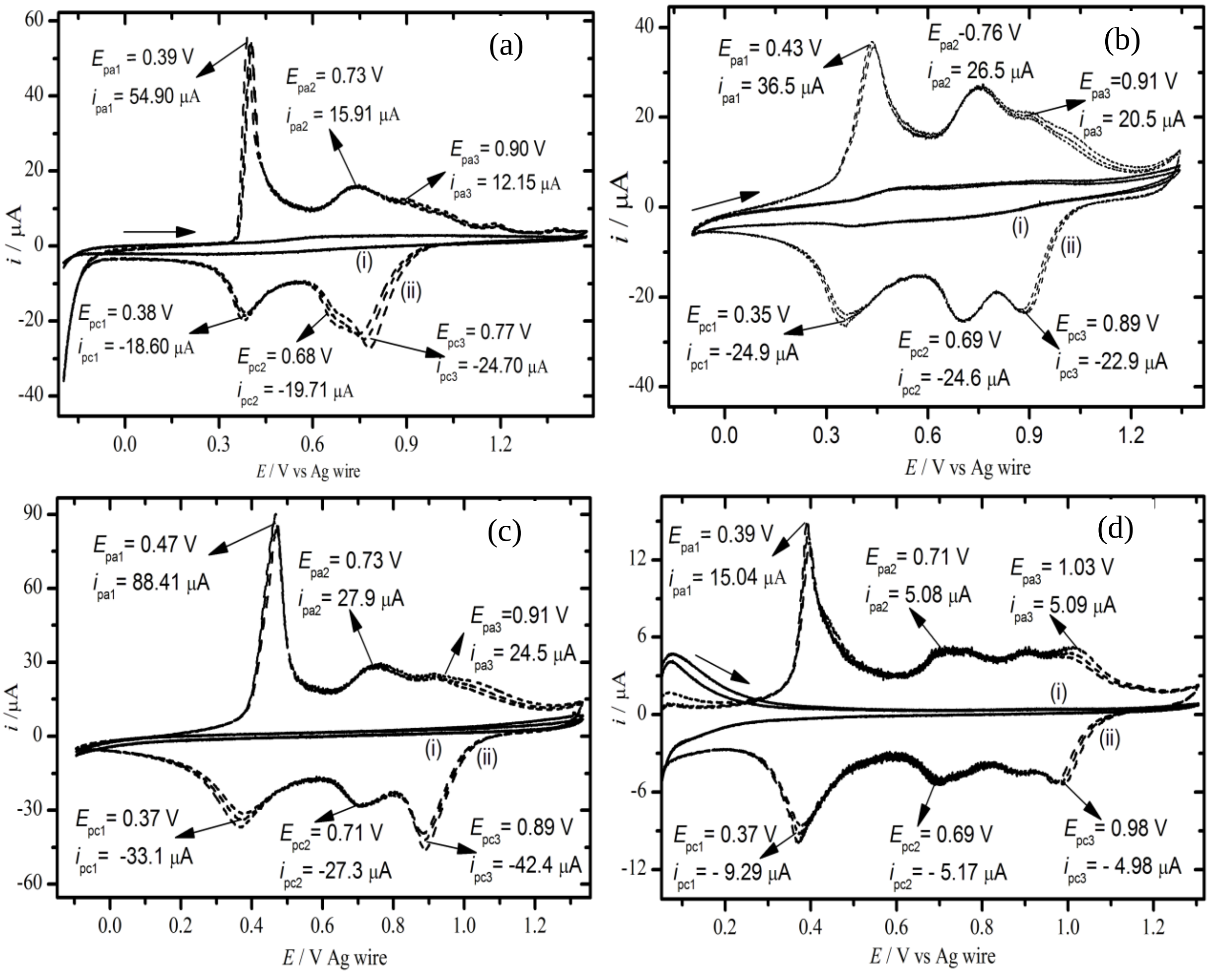
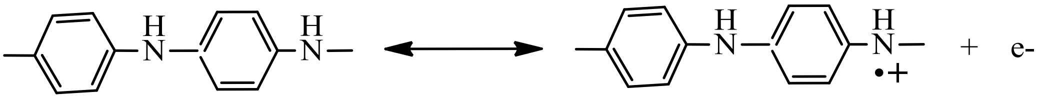
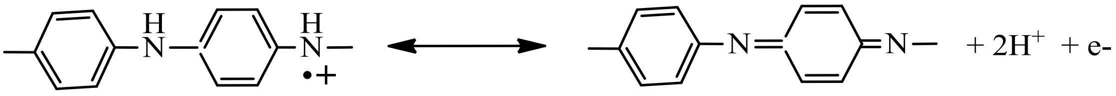


Figure 5. An overview of 3 CV cycles of (i) bare and (ii) PANI films on (a) Au, (b) GC, (c) PG and (d) Pt electrodes in 0.1 M HClO$_4$ /ACN at 50 mV s^{-1}.

Figure 5 is a display of the CVs of electropolymerized PANI films on each electrode in the same conditions. CVs of PANI deposited on each bare electrode are characterized by three main pairs of redox peaks. The redox peaks have been assigned using Pekmez formalism [47]: The first redox peak appearing between 0.36 and 0.45 V is the oxidation leucoemeraldine to leucoemeraldine radical cation interpreted by the following reaction:



The second redox peak is the emeraldine radical cation to emeraldine and the third redox peak between 0.8 and 1 V is the transformation of the pernigraniline radical cation to pernigraniline as shown in the following reaction:



While the middle peaks correspond to the intermediate reaction taking place. The overview of three cycles of CVs PANI show that the peak current and peak potential are constant which explains the excellent short time stability of the electrode *vis-à-vis* PANI. This property of stability gives to PANI good potential to be applied in the construction of sensors and biosensors.

The peak potential separation (ΔE_p) and the formal potential ($E^{o'}$) on each electrode were calculated and we observed that: ΔE_{p1}(Au) < ΔE_{p1}(Pt) < ΔE_{p1}(GC) < Δ(PG); ΔE_{p3}(PG) < ΔE_{p3}(GC) < ΔE_{p3}(Pt) < ΔE_{p3}(Au); $E^{o'}_1$(Pt) < $E^{o'}_1$(GC) < $E^{o'}_1$(Au) <$E^{o'}_1$(PG); $E^{0'}_3$(Au) < $E^{o'}_3$(PG) < $E^{o'}_3$(GC) < $E^{o'}_3$(Pt). Thus PG, Au and Pt electrodes have good characteristic vis-à-vis PANI; this can be accounted to their small values of peak separation ΔE_p and the Formal potential $E^{o'}$. The formal potential was taken as the average of the anodic and cathodic peak potential, $E^{o'} = (E_{pa}+E_{pc})/2$, the peak separation $\Delta E_p = E_{pa} - E_{pc}$. The ratio of the growth peak current (i_{pa3}/i_{pc3}) for each electrode was determine and it is approximately equal to 1 characterizing an irreversible system.

3.4. Reversibility of the system

The cyclic voltammogram diagnostics for an electrode reaction at the planar macroelectrode chemically involves stable and soluble redox couple: O + ne$^-$ $\rightleftarrows$ R. The above system can be reversible, quasi-reversible or irreversible. Figure 6 shows a series of voltammograms of PANI recorded on various electrodes at different scan rates in 0.1 M $HClO_4$/ACN were used to study the reversibility of the system. It was found that the peak current increase along with the rising of scan rate, while the ΔE_p expands slowly. In order to calculate the kinetic parameters of PANI redox on electrode surface, the scan rate was increased. The transfer coefficient α was calculated according to the slope of cathodic process (Figure 6 (II)) and we obtained 0.44 (Au), 0.31 (GC), 016 (PG) and 1.48 (Pt). According to the plot ΔE_{pc3} versus log ν (Figure 6(II)), the electrode reaction constant k_s per area of electrode of PANI films was calculated, 87.06, 0.28, 1.99, and 292.04 s^{-1} cm^{-2} for Au, GC, PG and Pt electrode respectively.

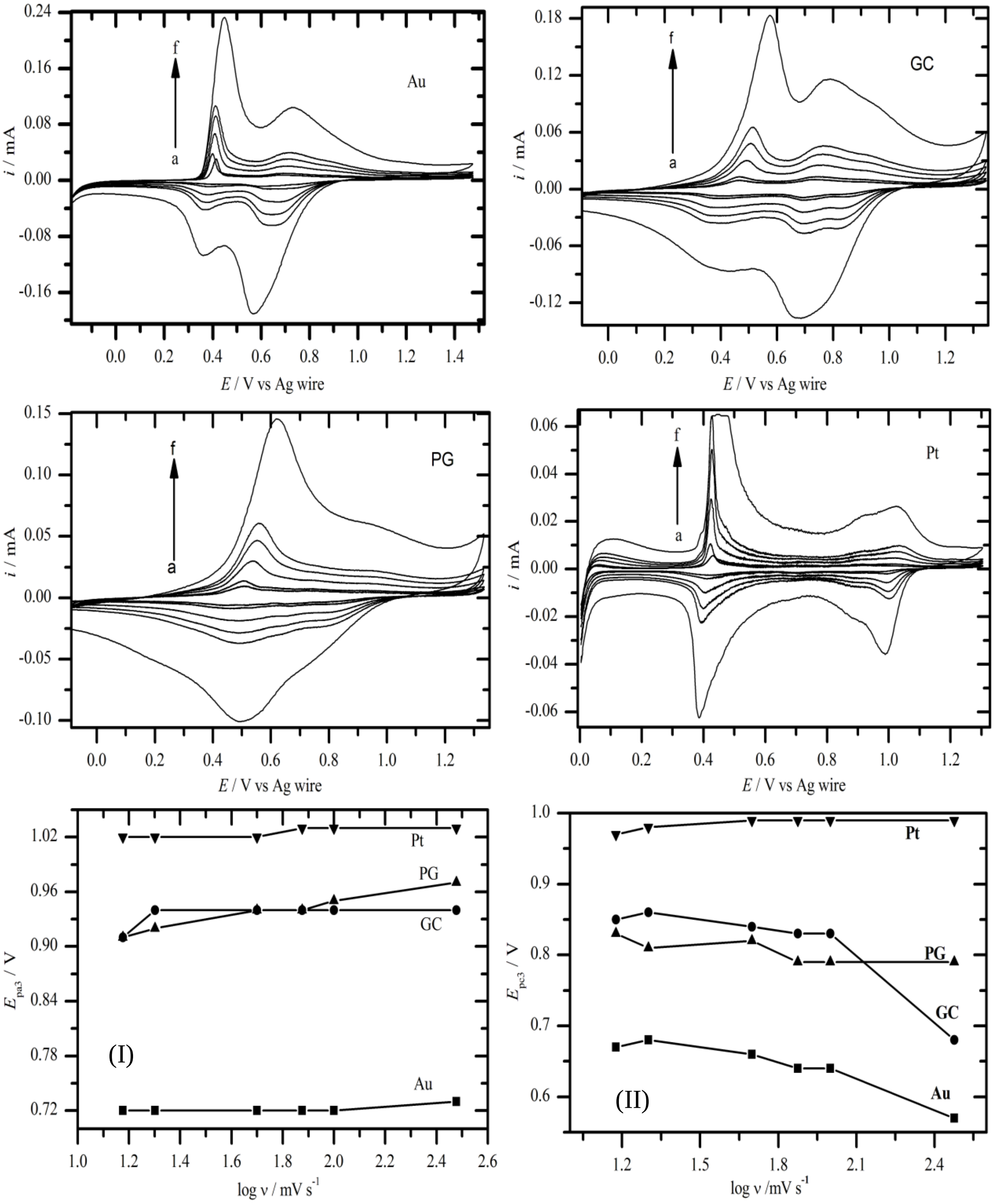


Figure 6. Cyclic voltammograms of the PANI modified-electrodes in 0.1 M $HClO_4$/ACN; potential scan rates: a) 15, b) 20, c) 50, d) 75, e) 100, f) 300 mV s^{-1} and on the bottom is the plot of the anodic (I) and cathodic (II) peak currents *vs*. log *v*.

It is seen that the value of k_s obtained on gold and platinum electrodes was very high compared to the result obtained in PANI prepared in 0.5 M H_2SO_4 on anodic aluminium oxide membrane as a template by Ziyi Wang *et al*. (5.8 s^{-1}) [48].

We observed three redox peaks for all electrodes and the peak potential remain the same when the scan rate is increased but, the peak current increases gradually. The fact that the peak potential is not shifted means E_p does not depend on the scan rate, thus, the system shows reversible electron transfer reaction.

For the application of PANI film in sensors, the study of the thickness of PANI films (thin or thick films) is reported. After electrochemical synthesis of the PANI films on the electrode surface, the voltammogram obtained was used to determine the peak potential and the peak current for each redox process taking place during the potentiodynamic growth of PANI films. The first cathodic peak which is implied on the study of the stability of the electrode *vis-à-vis* PANI was also used to determine the thickness of polymer film. Figure 7 shows the plot of the logarithm of PANI growth peak against logarithm of scan rates. The slope of the plot log $i_{pc\text{-}gr}$ *vs*. log ν was determined and approximately equal to 1 on each electrode, characteristic of PANI thin film.

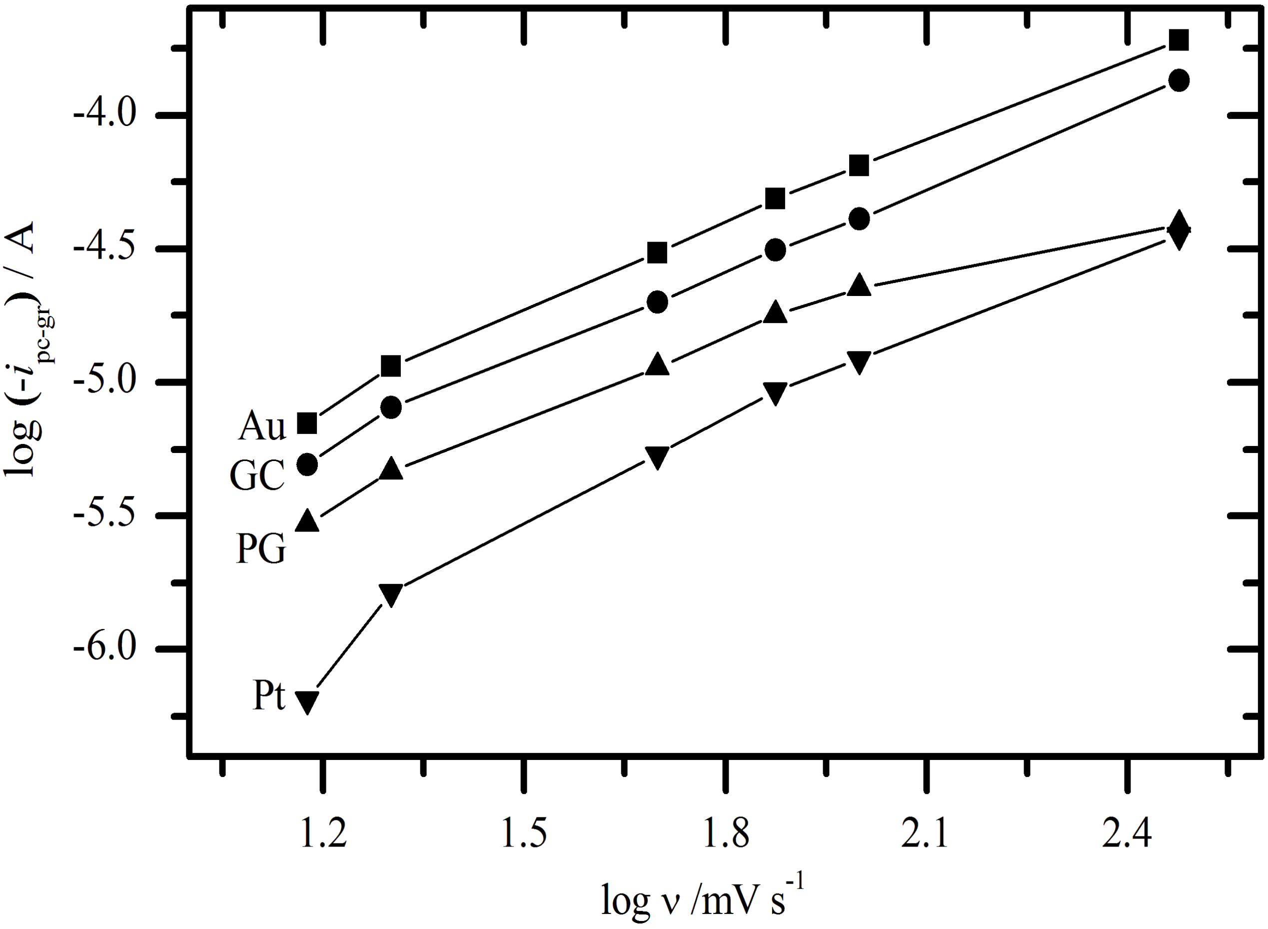


Figure 7. The plot of logarithm of the growing PANI peak i_{pc3} vs. log *ν*.

4. CONCLUSION

This paper has reported for the first time the electropolymerization of aniline on various electrodes (gold, glassy carbon, pyrolytic graphite, and platinum) in perchloric acid/acetonitrile at room temperature. The calculated value of the polymerization rate ($k_{\text{app-polym}}$) is proportional related to the quantity of the PANI formed on the electrode surface (Q_a). This demonstrated that more polymers are formed on PG and GC in organic medium than on Au and Pt electrodes. The CVs of PANI also showed regular peak potential and peak current during the voltammetric scan (3 cycles) which confirmed the good stability of the electrodes *vis-à-vis* PANI. From the results, PG and Pt have been chosen to be more suitable for electrodeposition of polyaniline in $HClO_4$/ACN at room temperature. All the information provided above can, therefore, be put in use as transducer in the development of electrochemical sensor platform.

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