

# Platinum Modified Poly 4-Aminoquinaldine Film Electrodes and Their Electrocatalytic Application in Oxidation of Small Organic Molecules

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The electrooxidation behavior of 4-aminoquinaldine (AQ) in H<sub>2</sub>SO<sub>4</sub> was investigated by sweep potential method. The resulting polymeric film has poor redox response in NaCl aqueous electrolytic solution. After soaking the polymeric film in CuCl<sub>2</sub> aqueous solution for 45 minutes, the resulting loaded polymer film has a dramatic waves when tested in the same electrolytic solution. A well defined redox response was obtained and exhibited a thin layer behavior. The electrocatalytic activity of the modified electrode for the oxidation of methanol, propanol and formaldehyde in aqueous acidic solution was studied by using cyclic voltammetry. Results showed that, poly AQ/Pt modified electrode can improve the activity of Pt towards the oxidation of these small organic molecules, showing the possibility of attaining good electrocatalytic anodes for fuel cells.

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**Keywords:** 4-aminoquinaldine, Cyclic voltammetry, Electrooxidation, Electrocatalysis, Modified electrode, Electrochemical stability.

## 1. INTRODUCTION

Modifying electrode surfaces with polymer containing species is an extremely attractive method for controlling the chemical and electronic properties of electrodes [1-5], in addition to possible application to electrocatalysis, sensors, ect. [6-13]. A redox polymer film which would allow both diffusion of the reactants and charge propagation through the film with reasonable rates is expected to be a much better mediation catalyst than the soluble mediator itself on bare electrodes. Another strategy for redox polymer film formation is to deposit polymer films having the ability to fix the redox species from solution via electrostatic attraction or complexation [4,5], to improve the redox response, electrocatalytic activity and stability of the polymer film. On the basis of the preliminary studies reported previously [14], we report here the electropolymerization of AQ in aqueous medium,

and study the experimental condition, the catalytic behavior of the polymer film formed and a probable mechanism of charge transport for charging and discharging process is advanced. Moreover, the electrocatalytic properties of poly AQ/Pt modified electrodes will be considered.

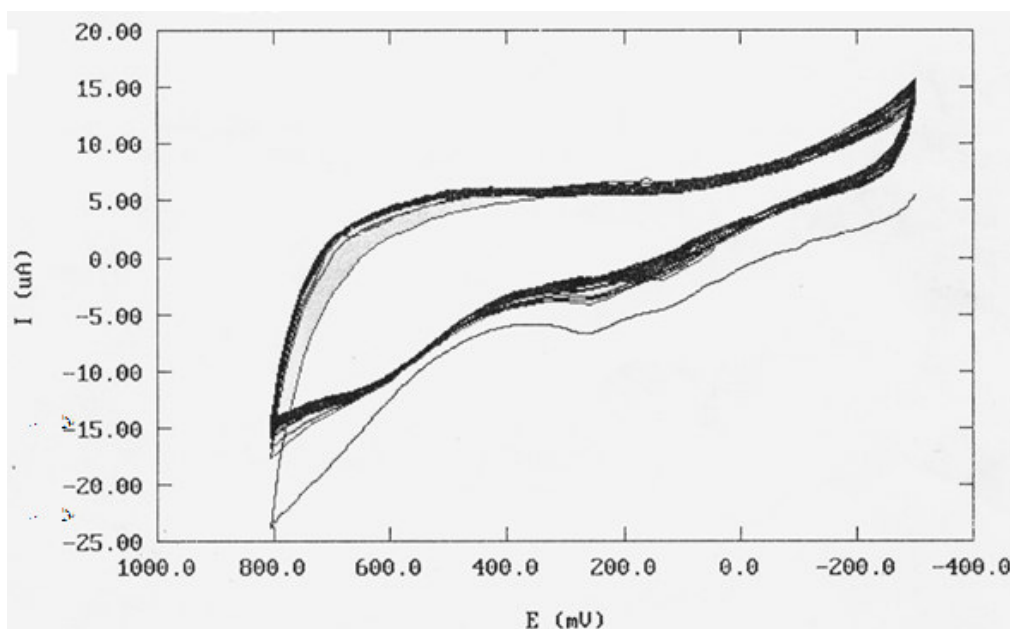
## 2. EXPERIMENTAL PART

4 - aminoquinoline, lithium perchlorate, acetonitrile, methanol, propanol, formaldehyde, sodium chloride and sulfuric acid were analytical grade chemicals (Aldrich) and used without further Purification. Aqueous solution was prepared from bidistilled water. Electrochemical measurements were carried out using the EG&G PAR computer measuring system (model 250) and potentiostat CV 50w and X-Y Hewlett-Packard recorder (model 7440). A three electrode electrocatalytic cell (bioanalytical system, model C-1A) with a platinum disc electrode (Pt) 3.0 mm diameter was used as working electrode, a platinum sheet as a counter electrode and formation.

## 3. RESULTS AND DISCUSSION

### 3.1. Electrooxidation of 4-aminoquinoline and film formation

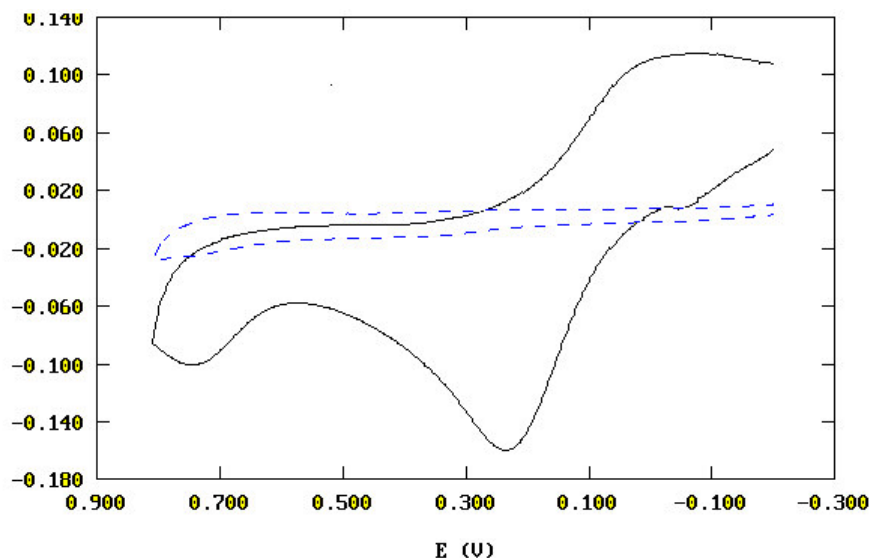
Cyclic voltammograms of the synthesis of poly AQ recorded in a potential range between  $-0.3$  and  $0.8$  V using sweep rate  $0.1$   $\text{Vs}^{-1}$  on Pt electrode, from aqueous solution containing  $10^{-3}$  M AQ and  $0.2$  M  $\text{H}_2\text{SO}_4$  was shown in Fig.1. The first cycle shows an irreversible oxidation anodic peak at  $0.22$  V. On repeating the potential scan after the first cycle, the height of the oxidation peak decreased which suggest that during the first cycle the electrode is coated with an insulating film.



**Figure 1.** Consecutive cyclic voltammograms of poly 4-aminoquinoline (AQ) film growth on a platinum electrode in  $0.2$   $\text{H}_2\text{SO}_4$  at a scan rate of  $0.1$   $\text{V/s}$ . Concentration of  $\text{AQ}=10^{-3}$  M and potential range =  $-0.3$  to  $0.8$  V.

### 3.2. The redox response of the polymeric film

Examination of the electrode surface after its potential cycling showed the formation of polymeric film with interference colors. In the absence of AQ, the platinum electrode covered by poly AQ films, shows no redox response in electrolytic aqueous medium. Fig. 2a shows the voltammetric response of the polymer film in 0.2 M NaCl. The electrodes covered by polymer films were immersed in 0.7 M  $\text{CuCl}_2$  solution for 45 minutes then washed thoroughly with  $\text{H}_2\text{O}$  and tested in 0.2 M NaCl (Fig. 2b), which shows the activity of the loaded polymer film of poly AQ on Pt electrode. The loaded polymeric film shows a pair of redox response peak at 0.2 and 0.0 V for anodic and cathodic peaks respectively. It is noticed that the surface – immobilized redox species binds Cu (II) ions films. The electrode exposed to the copper solution shows a pair of redox peaks. The cyclic voltammogram of surface – bound  $\text{Cu}^{+2}$  is similar to that of free  $\text{Cu}^{+2}$ , which shows a broad cathodic and a sharp anodic wave characteristic of metal deposition and stripping respectively [1,15,16].



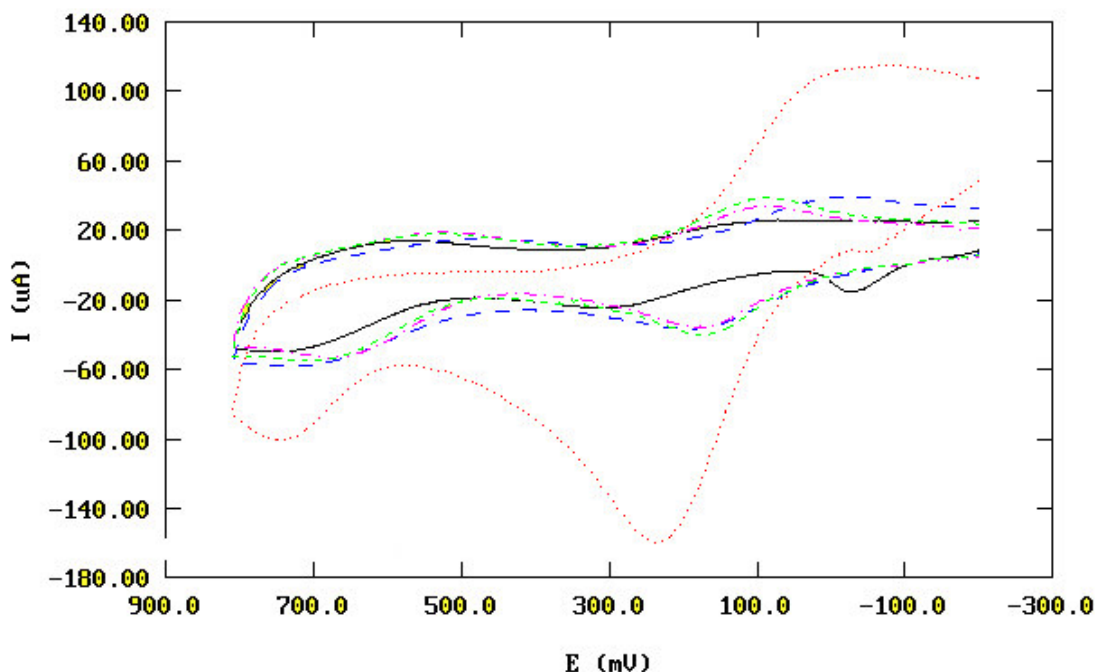
**Figure 2.** Cyclic voltammogram of poly AQ/pt electrode in 0.2 M NaCl aqueous at scan rate 0.1V/s, the film formed as mentioned in Fig. 1 a) - - - activity of the modified electrode in 0.2 M NaCl without soaking and b) — activity of the modified electrode in 0.2 M NaCl after soaking in 0.7M  $\text{CuCl}_2$  for 45 minutes.

### 3.3. Factors influencing the electrochemical response of poly AQ/Pt modified electrodes.

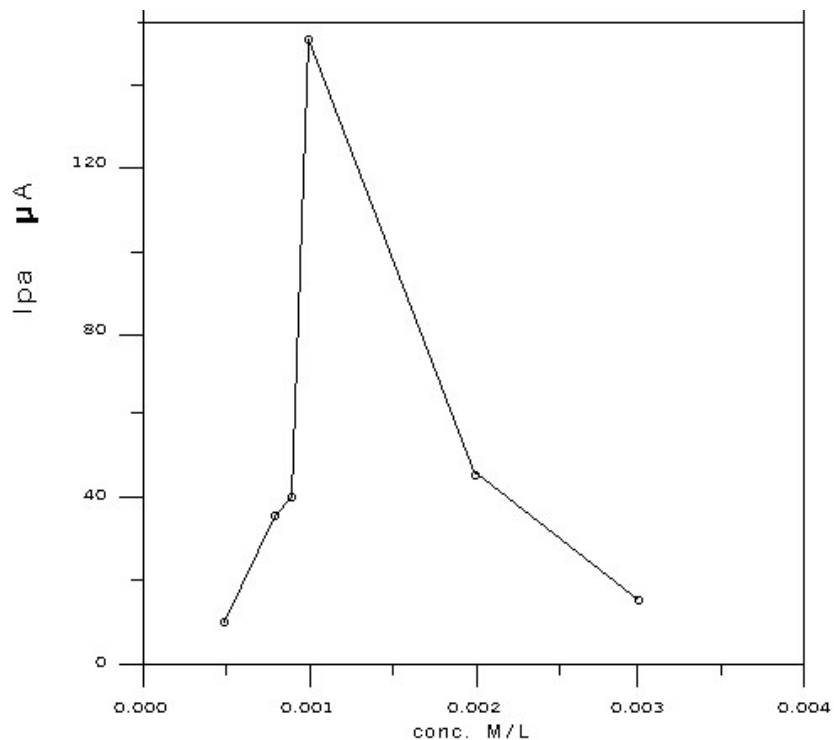
#### 3.3.1 Effect of monomer concentration during polymerization process.

The redox response of the loaded poly AQ/Pt modified electrode in 0.2 M NaCl was found to be dependent on monomer concentration during film formation, and the relationship between the current response and AQ monomer concentration is shown in Fig. 3a. With the increment of AQ concentration, the response current  $I_{pa}$  increased, when the AQ concentration is less than  $10^{-3}$  M, but it decreased gradually when AQ Concentration is higher than  $10^{-3}$  M. Fig. 3b. This illustrates

that too high AQ concentration may result in thick and compact films, which don't facilitate the redox process. Therefore, in this work, a moderate AQ concentration  $10^{-3}$  M was selected for preparation of poly AQ/Pt modified electrode [17-20].



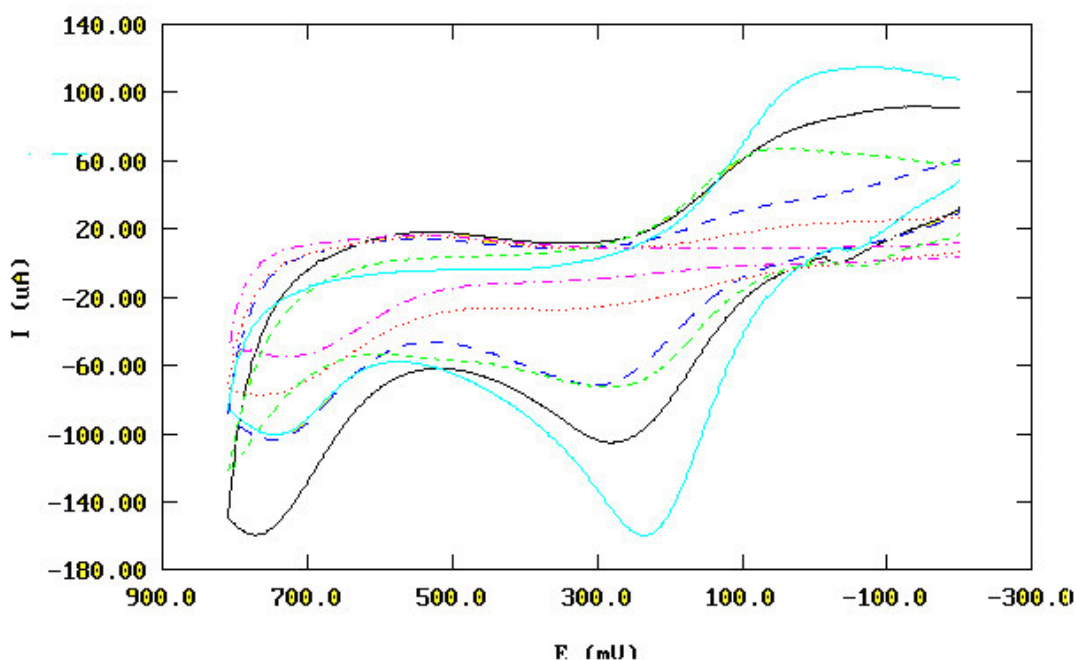
**Figure 3a.** Effect of monomer concentration during film formation on electrochemical response of polymer; —  $3 \times 10^{-3}$  M/L, - - -  $2 \times 10^{-3}$  M/L, .....  $1 \times 10^{-3}$  M/L, - · - ·  $9 \times 10^{-4}$  M/L and .....  $8 \times 10^{-4}$  M/L



**Figure 3b.** Effect of 4- aminoquinoline concentration on anodic peak current  $I_{pa}$ .

### 3.3.2. Effect of sulfuric acid concentration during polymerization process.

It was found that the redox response of the loaded poly AQ/Pt modified electrodes, depends on  $\text{H}_2\text{SO}_4$  concentration during film formation. The study was carried out at different acid concentration containing  $10^{-3}$  M of monomer. The electrode was swept in potential range from -0.3 to 0.8 V at scan rate  $0.1 \text{ Vs}^{-1}$  for 20 cycles. Fig. 4 shows the redox response of the loaded poly AQ/Pt modified electrode prepared in different acid concentrations, in 0.2 M NaCl. It was found that the current response increases as the acid concentration increase in polymerization bath upto 0.2 M, further increase in acid concentration was followed by a marked drop in the redox response of modified electrode. This could be attributed to the partial degradation of the film in presence of high acid concentration [20,21].

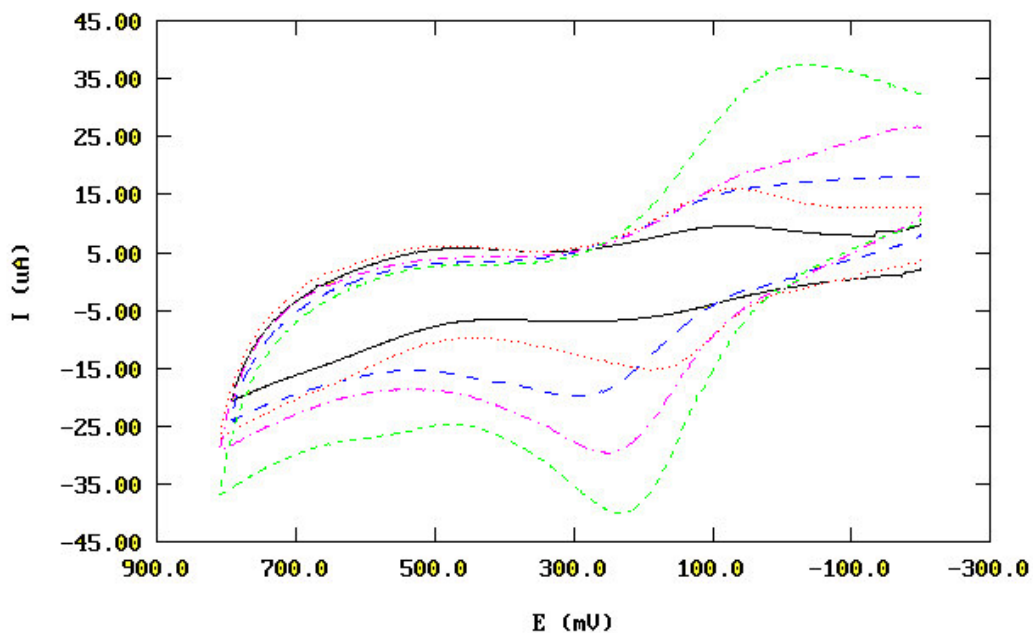


**Figure 4.** Effect of  $\text{H}_2\text{SO}_4$  concentration during film formation; — 1M, - - - 1.5M, ..... 0.1M, - · - · 0.7M and - · - · 0.5M and — 0.2M

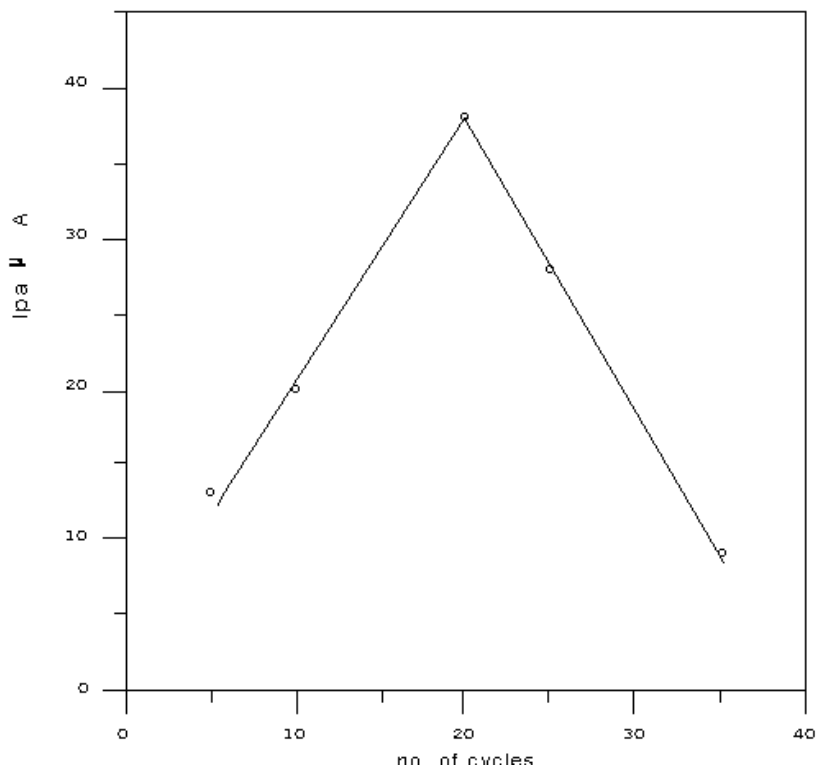
### 3.3.3. Effect of film thickness

The effect of film thickness, determined by the number of polymerization scans, on the electro activity and stability of the loaded poly AQ/Pt modified electrode, was studied on film electrodes prepared in an aqueous acidic solution containing 0.2 M  $\text{H}_2\text{SO}_4$  and  $10^{-3}$  M of AQ monomer, by different number of cycles ranging from 5 to 30. Fig. 5a shows cyclic voltammetric response of the loaded poly AQ/Pt electrode in 0.2 M NaCl. The relation between the anodic peak current  $I_{pa}$  of loaded poly AQ/Pt modified Electrode and the number of cycles used in the polymer formation, can be seen in Fig. 5b.  $I_{pa}$  increases with the increasing the number of cycles up to 20, further increase in the cycles the current decrease. This behavior indicates the diminishing of the polymerization

process as the polymer film increases, most probably due to the retardation of the electron transfer through the barrier – type polymer films, thus, thick polymer films can't be prepared [3,21].



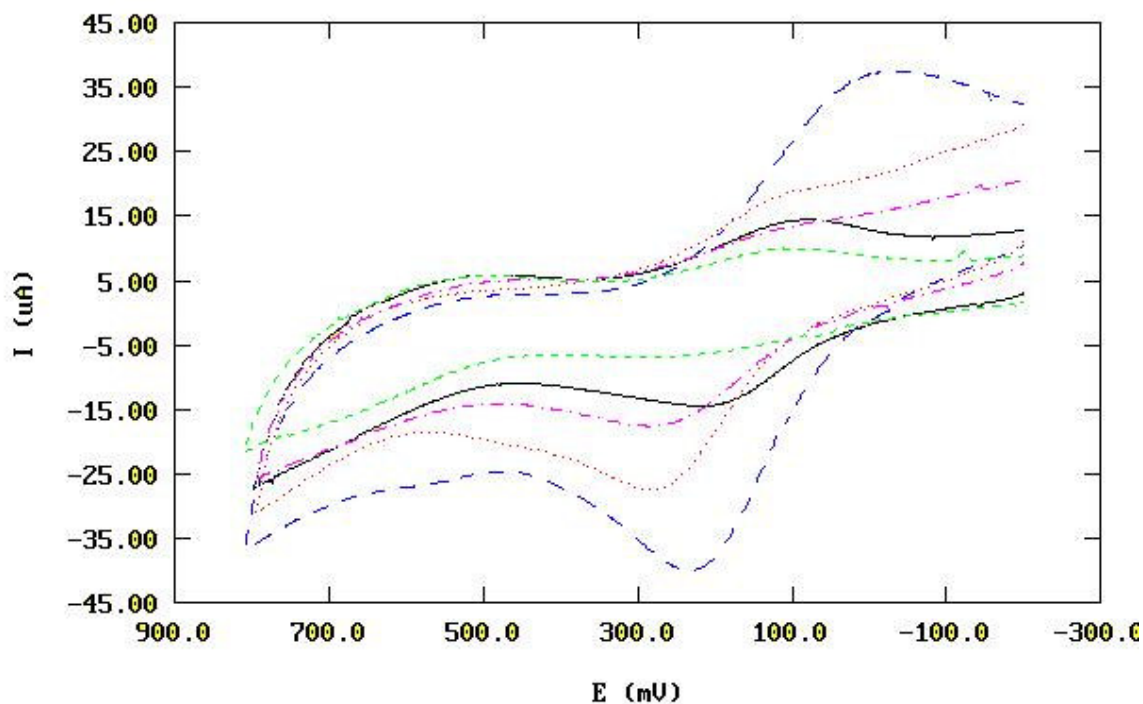
**Figure 5a.** Effect of film thickness of the loaded poly AQ/Pt electrode in 0.2 M NaCl; — 35 cycles, - - - 10 cycles, ..... 5 cycles, - - - 20 cycles and - · - · 25 cycles.



**Figure 5b.** Effect of film thickness on anodic peak current Ipa.

### 3.3.4. Effect of potential limits during film formation.

The limits of potential cycling applied for film formation affected greatly the redox response of the resulting modified electrode. Fig. 6 shows the cyclic voltammetric responses of the loaded poly AQ/Pt modified electrodes prepared by sweeping the working electrode for 20 cycles between different potential limits. Comparison of the redox current response reveals that the film electrode prepared by potential sweeping from -0.3 to 0.8 V is the most electro active one. Therefore, increasing the positive potential up to 0.8 V reduces both the film stability and the current of its response as shown in Fig. 6. On the other hand, lower positive potential than 0.8 V is not suitable for the preparation of stable electro active films [20-23].



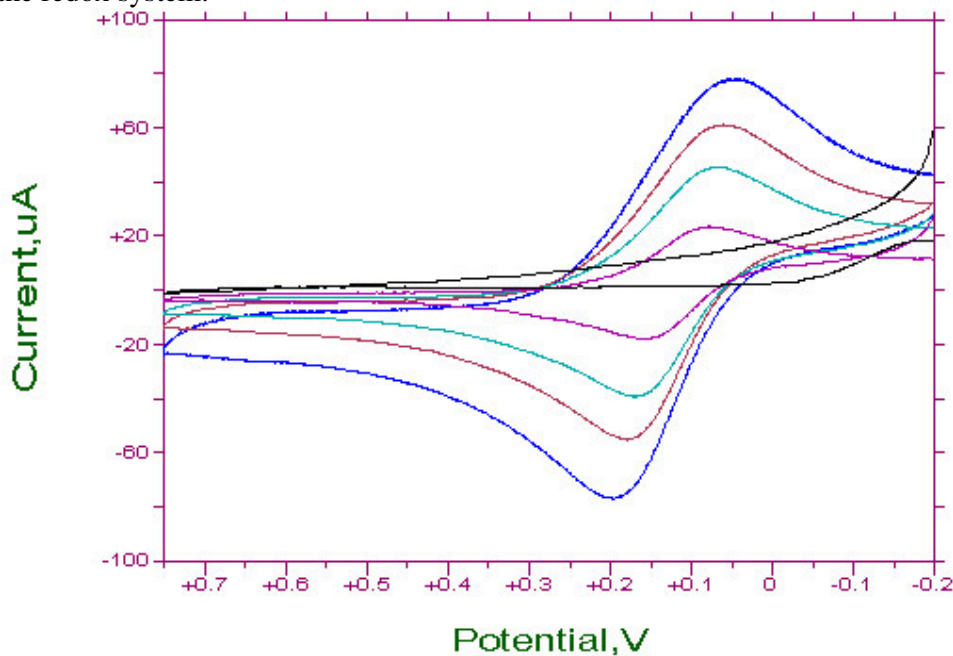
**Figure 6.** Effect of potential range during the film formation; — -0.1 to 0.8V, ..... -0.2 to 0.8V  
 - - - - -0.3 to 0.8V, - · - · -0.3 to 0.9V and - - - - -0.3 to 0.7V

### 3.3.5. Effect of scan rate

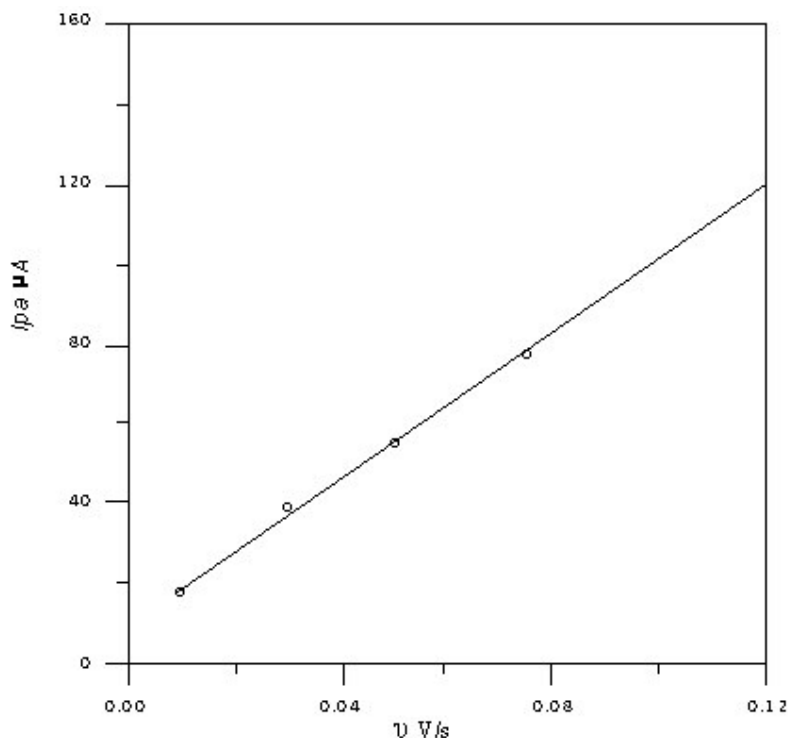
The effect of scan rate potential on the electrochemical behavior of the loaded poly AQ/Pt modified electrode was studied in 0.2 M NaCl aqueous solution by cyclic voltammetry (Fig. 7a). The plot of the anodic peak current,  $I_{pa}$ , against the scan rate (Fig. 7b) showed that, the  $I_{pa}$  values was linearly dependent on scan rate. The ratio of  $I_{pa} / I_{pc}$  remains almost equal unity. This typical behavior of a strongly attached, electrochemically active site and was intensively reported for thin layer film of conducting and redox polymers [18,22-24]. Fig. 7c illustrates the relation between the peak separation ( $\Delta E_p = E_{pa} - E_{pc}$ ) and scan rate, as expected,  $\Delta E_p$  increases with scan rate, due to both



the polymer film resistance and the uncompensated electrolyte resistance [3,25]. On the other hand, at higher or fast scan rate (starting from  $150 \text{ mV}^{-1}$ ), the peak currents are proportional to the square root of the scan rate [20,26], indicating that the reaction is diffusion-limited (Fig.7d). The excellent stability of the modified electrode over 200 continuous cycling between -0.2 and 0.8 V in 0.2 M NaCl solution, should be emphasized. Only a slight decrease of about 10% of both anodic and cathodic peak currents of the redox system.

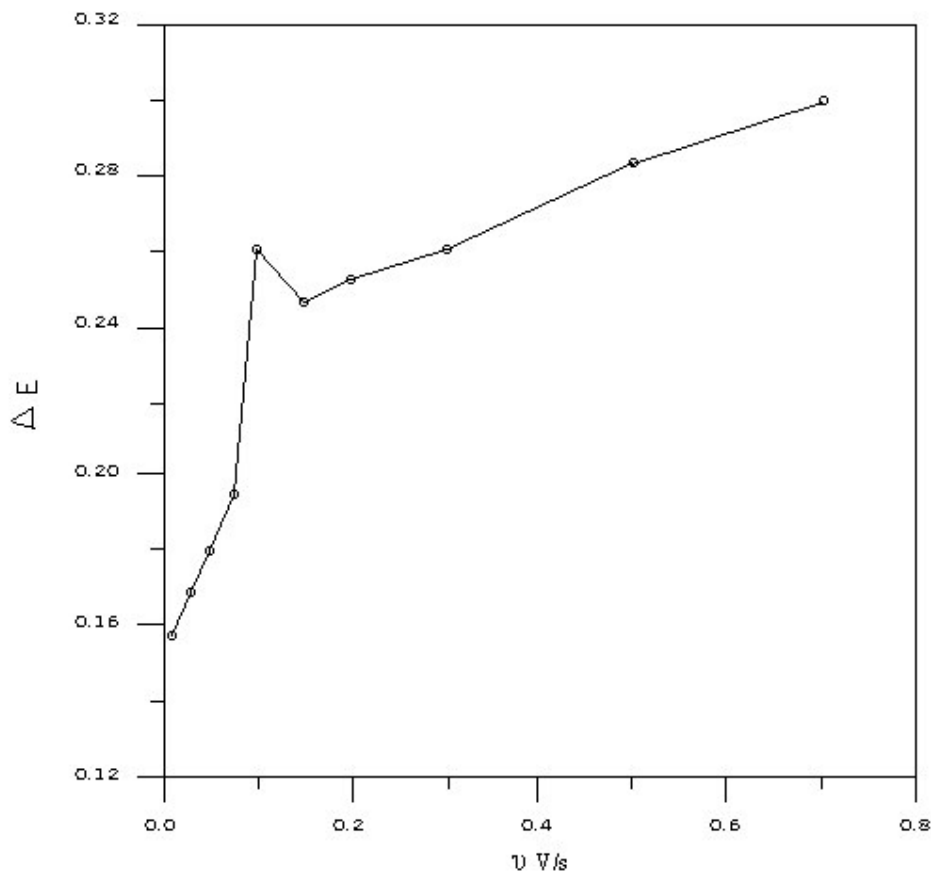


**Figure 7a.** Effect of low scan rate after film formation; — 5 mV/s, — 10 mV/s, — 30 mV/s, — 50 mV/s and — 75 mV/s.

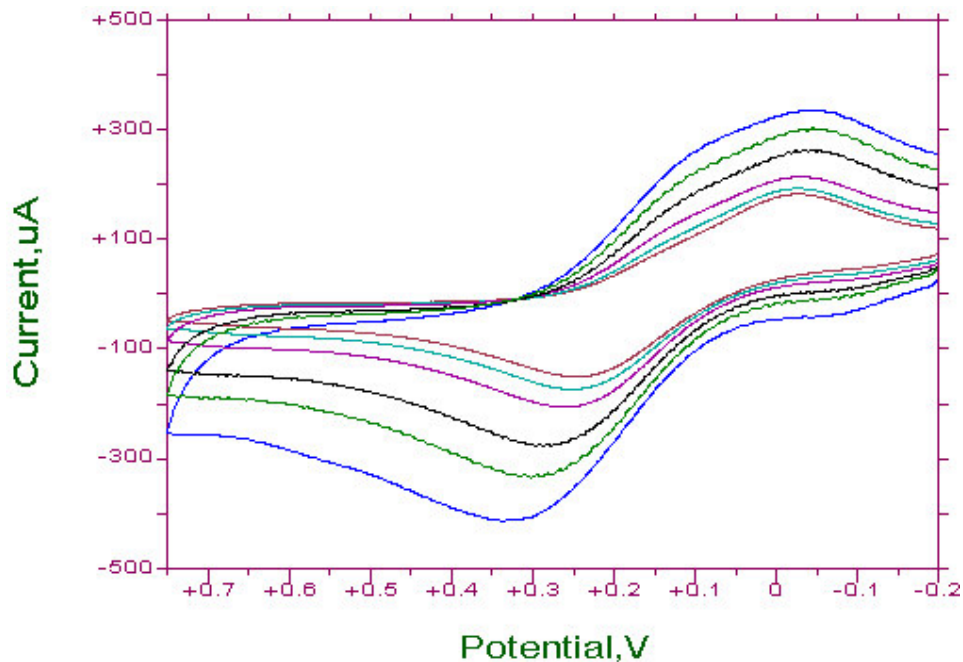


**Figure 7b.** Effect of scan rate  $v$  on anodic peak current  $I_{pa}$ .

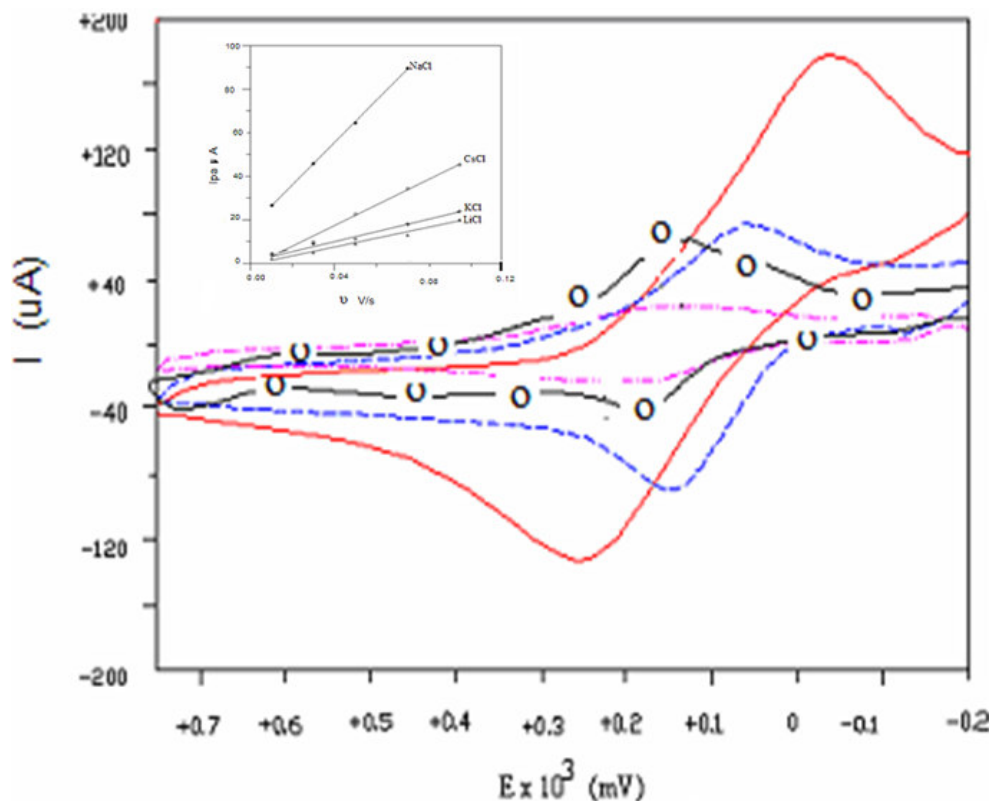




**Figure 7c.** Effect of scan rate  $v$  on the peak separation  $\Delta E$ .



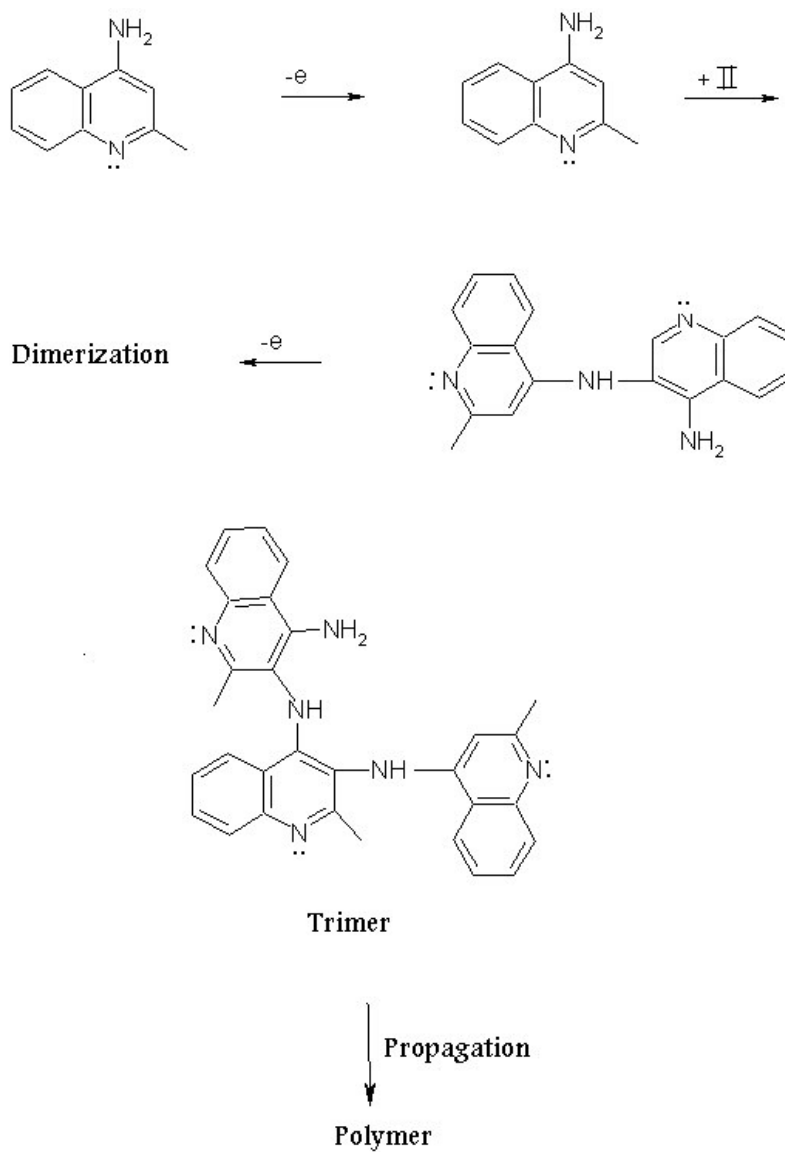
**Figure 7d.** Effect of high scan rate after film formation; — ) 150 mV/s, — ) 200 mV/s, — ) 300 mV/s, — ) 500 mV/s, — ) 700 mV/s and — ) 1000 mV/s.



**Figure 8.** Effect of cations of electrolyte on the response of the film; — 0.2 M NaCl, — 0.2 M CsCl, — 0.2 M KCl and — 0.2 M LiCl, the inset shows the effect of supporting electrolyte scan rate  $v$  on anodic peak current  $I_{pa}$ .

### 3.3.6. Effect of supporting electrolyte.

As expected, the cation of the supporting electrolyte is involved in the redox response. Fig. 8 presents comparative cyclic voltammograms for the loaded poly AQ/Pt modified electrode in 0.2 M supporting electrolytes containing various alkali metal cations, LiCl, NaCl, CsCl and KCl. It is well known that the counter ions influence the voltammetric behavior of the electrode, and the redox couple were cation dependent. The investigation of the cyclic voltammetric characteristics of the loaded poly AQ/Pt modified electrode in different supporting electrolyte suggested the following permeability of cations  $\text{Na}^+ > \text{Cs}^+ > \text{K}^+ > \text{Li}^+$  except for  $\text{Na}^+$  the trend follows the increment in solvated ionic radii [26-28]. Indeed, the insertion process can't be exactly explained in accordance with the hydrated ionic. In other words, although, the relationship of the hydrated ionic radii and the lattice channel size is of importance to understand the electrochemical behavior of the system under investigation in the presence of various supporting electrolyte, however other factors may also involved [24]. The inset, shows the relation between supporting electrolyte concentration and the anodic peak current ( $I_{pa}$ ) in each case at different scan rate.

**Scheme 1.**

### 3.4. Polymerization mechanism

On the basis of the above experimental results, the proposed structure of the polymer and polymerization mechanism is given in scheme 1. The polymerization can proceed via either radical/radical coupling or radical cation/monomer coupling followed by further oxidation of the dimer, trimer,...ect., and deprotonation. This mechanism is confirmed with their spectrum of the obtained film, so absorption peaks at  $3300 - 3500 \text{ cm}^{-1}$  (NH stretching),  $1670 - 1680 \text{ cm}^{-1}$  (C=N bonds) and  $1300, 1720 \text{ cm}^{-1}$  (secondary aromatic amines), this agrees that the polymerization occurs via the formation of C-N=C and C-NH-C. [3,4,14,21,29]. Moreover the electropolymerization of AQ was carried out in presence of  $\text{Cu}^{+2}$  in polymerization bath and the redox response of the resulting polymer film was measured in 0.2 M NaCl. The film give poor redox response which reflect that  $\text{Cu}^{+2}$  can't

inter in the polymer matrix, and it can be immobilized on the surface of the polymer film after soaking it in  $\text{CuCl}_2$  solution. This coincides with the presence of a lone pair of electron on the nitrogen atom of the hetero ring and also the presence of  $-\text{CH}_3$  group in ortho position which is a releasing group enhancing the electron density on this nitrogen atom to bind  $\text{Cu}^{+2}$ .

### 3.5. *Electrocatalytic behavior*

The electrochemical oxidation of small organic molecules is of fundamental importance in electrocatalysis, and it is also a key factor understanding alcohol oxidation for fuel cell applications [30-33].

#### 3.5.1. *Electrocatalytic oxidation of methanol*

Fig. 9 shows the voltammogram for the electrooxidation of 0.2 M methanol at a bare and unloaded and loaded modified Pt electrodes in 0.2 M HCl aqueous solution. The figure illustrates that, there is an appearance of anodic peak at .18V and corresponding cathodic peak at .1 V in case of loaded modified electrode compared to unloaded modified and bare electrodes.

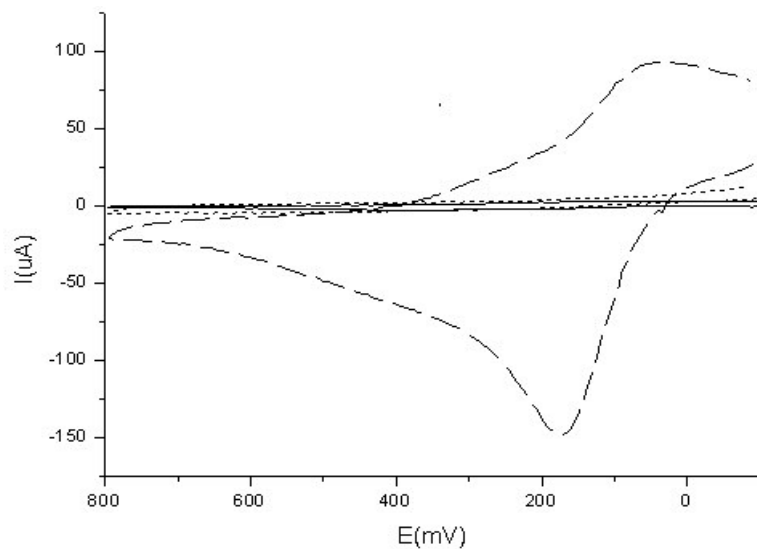
#### 3.5.2. *Electrooxidation of propanol*

The electrooxidation of propanol in 0.2 M HCl on bare, unloaded modified and modified Pt electrodes was shown in Fig. 10. We can observe that, in case of loaded modified electrode an anodic peak appear at .2 V and a broad cathodic peak appear at .1 V. While there's no response in case of unloaded modified and bare Pt. electrodes.

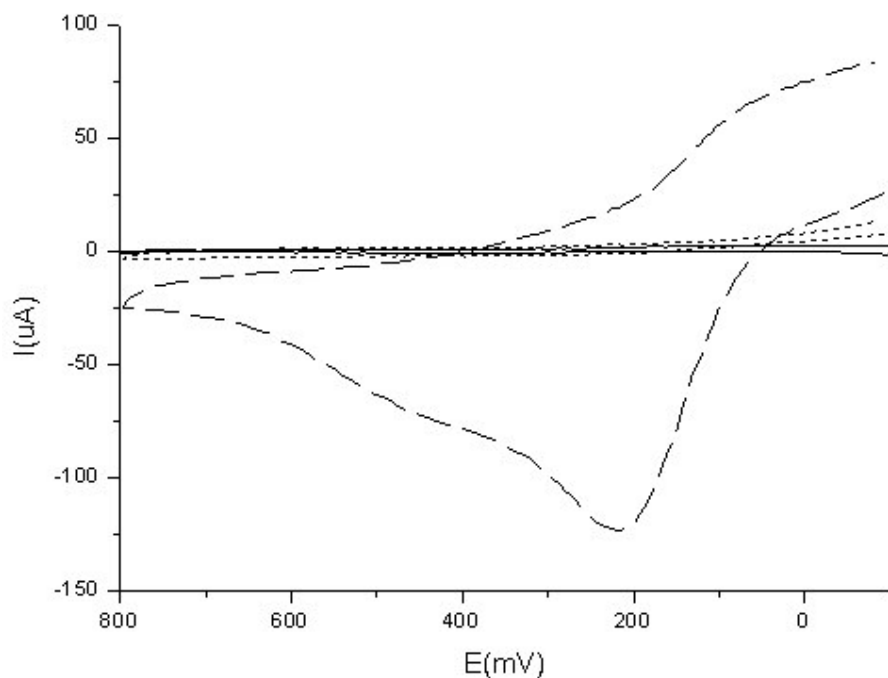
#### 3.5.3. *Electrooxidation of formaldehyde*

Fig. 11 illustrates the improvement in the electrooxidation process on the loaded modified electrode with respect to the unloaded modified and bare Pt. electrodes for the formaldehyde acid in 0.2 M HCl aqueous solution. The Fig. shows that the electrooxidation of formaldehyde on unloaded and bare electrode give no response, while on loaded modified electrode, two anodic peak appear first at .2 V and the second at .5 V and one broad cathodic peak at .95 V.

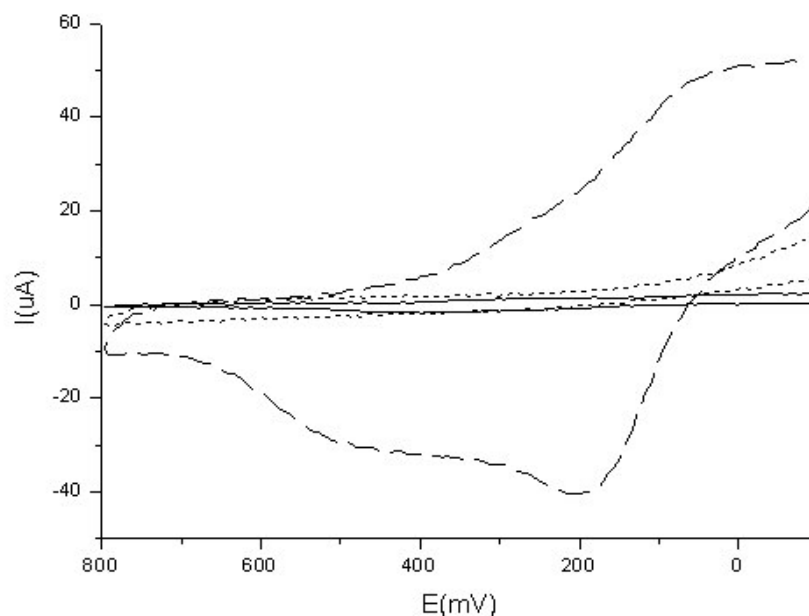
The obtained results clearly show that loaded poly AQ/Pt modified electrode presented good improvement for electrocatalytic oxidation of small organic molecules e.g methanol, propanol and formaldehyde compared to bare electrode. The electroactivity of such an electrode towards the oxidation of these small organic molecules is very encouraging, showing the possibility of attaining good electrocatalytic anodes for fuel cells [34].



**Figure 9.** . Catalytic behavior of 0.04 M methanol in 0.2 M HCl, — — loaded poly AQ/Pt modified, ----- unloaded poly AQ/Pt modified and ..... bare Pt electrodes. The other details as in Fig. 1.



**Figure 10.** . Catalytic behavior of 0.04 M propanol in 0.2 M HCl, — — loaded poly AQ/Pt modified, ----- unloaded poly AQ/Pt modified and ..... bare Pt electrodes. The other details as in Fig. 1.



**Figure 11.** Catalytic behavior of 0.04 M formaldehyde in 0.2 M HCl, ——— loaded poly AQ/Pt modified, - - - - - unloaded poly AQ/Pt modified and ..... bare Pt electrodes. The other details as in Fig. 1.

#### 4. CONCLUSIONS

The oxidative polymerization of 4-aminoquinoline in sulfuric acid aqueous solution has been successfully performed by electrochemical method. It should be noted that the condition for preparing the film do influence its properties. The best quality films are produced in  $10^{-3}$  M monomer concentration, 0.2 M sulfuric acid concentration, in potential range from -0.3 to 0.8 V at scan rate  $0.1 \text{ V s}^{-1}$  and soaking in 0.7 M  $\text{CuCl}_2$  for about 45 minutes. Therefore, the unloaded film exhibits a poor redox response, but after loading, a well defined redox response appeared in 0.2 M NaCl. It was found that the voltammetric response of poly AQ/Pt modified electrode is affected by the type and the concentration of the supporting electrolyte. Poly AQ/Pt modified electrode presented a good catalytic activity towards the oxidation of small organic molecules e.g. methanol, propanol and formaldehyde showing the possibility of attaining good electrocatalytic anodes for fuel cells.

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