EFFECT OF ELECTRODE NATURE ON THE ELECTRO POLYMERIZATION AND ELECTROCHEMICAL BEHAVIOR OF 8(3-ACETYLIMINO-6-METYL 2,4 DIOXOPYRAN) 1-AMINONAPHTHALENE

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ABSTRACT

This article describes the electro synthesis of poly 8(3-acetylimino-6-metyl 2,4- dioxopyran) 1-aminonaphthaline. (PAMDAN) on Pt (PAMDAN/Pt) and GC (PANDAN/GC) electrodes from 0.1M H_2SO_4 aqueous solution. Fairly stable films of PAMDAN were obtained on both electrodes, the oxidation potential and the current density of the monomer depends of the nature of the electrode substrate, the redox response of both polymer films was examined in 0.1 M H_2SO_4 at different scan rate and the stability was studied by cyclic voltammetry. The polymer films show a good catalytic behavior and the obtained data illustrate that the nature of the electrode substrate play an important role in the behavior of the obtained modified electrodes.

1- INTRODUCTION

Conducting polymers (CP) have been extensively studied during the last 20 years in view of their potential application for example as capacitors, sensors, fuel cells, protection against corrosion, electrocatalyist and other applications. The possibility of a polymer film formed directly on a metal was obtained mostly by the polymerization of appropriate monomers. The physical and chemical, properties (stability,

conductivity, morphology, structure and catalytic activity) of various CP were carefully studied by many researchers **[Skotheim (1986); Heinze et al., (1990); Simonet et al., (1991) and Rubinson (1999)]**. It has been established that the polymer layers behavior depend on the condition of the electro polymerization process (potential, current density and temperature) and as well on the composition of the electrolyte **[Lyons et al., (1996); Nalwa (1997); Malinauskas (1999) and Inzelt et al., (2000)]**. The electro deposition of CP is also depends on the metal substrate, it was found that the oxidation potential of the monomer varied by using different substrate **[Prejza et al., (1982) and Cheung et al., (1988)]**. However, the morphology of the polymer film was depends on the kind of the metal substrate **[Cheung et al., (1988) and Zalewska et al., (2000)]**. In this connection, the present study aims to study the electrochemical behavior of PAMDAN using two different electrodes Pt and GC by cyclic voltammetry(CV)

2-EXPERIMENTAL

Materials: 1,8- diaminonaphthalene. dehydroacetic acid, hydroquinoue and sulfuric acid were of analytical grade chemicals (Aldrich) and were used without further purification. Aqueous solutions were prepared by bidistilled water. Electrochemical measurements were performed using the EG & PAR computer measuring system model (250) and a Hewlett-packard X-Y recorder model (7440). A three-electrode electrolytic cell (Bioanalytical system, model (C-lA) with a platinum disc electrode (Pt) (3.0 mm diam), and glass carbon (GC) were used as working electrode. A platinum sheet was used as counter electrode and Ag/AgCl electrode as a reference electrode was used.

AMDAN Schiff 's base was prepared and characterized according to reported method **[Abd El-Rahman et al., (2000)]**, and its the structure is shown in Fig .1
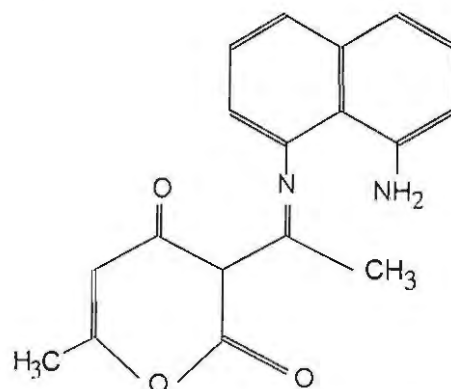
Fig. (1): 8(3-acetylimino-6- metyl-2,4-dioxopyran)-1-aminoaphthalene (AMDAN)

3-RESULTS AND DISCUSSION

1- Cyclic voltammetry and film formation

Fig.2 a, b show the consecutive voltammograms in 0.1 M H_2SO_4 aqueous solution containing 2×10^{-3} M AMDAN Shiff Base on Pt and GC. The figure illustrate that the monomer was oxidized in an irreversible manner and give one oxidation peak during first scan and one reduction peak. On scan repetition the oxidation peak diminished and a new redox system was appeared due to polymer deposition at electrodes surface [**Abd El-Rahman et al., (2000); Yousef et al., (2001) and Diab et al., (2000)**].

The oxidation potential and the anodic peak current of AMDAN monomer was found to be varied with the electrode material [**Cheung (1988) and Biallozor (2005)**] as shown in Fig .2(a,b): The quantitative data is listed in Table 1

Table (1): Redox potentials (E_{pa}, E_{pc}) and current intensities (i_{pa}, i_{pc}) of AMDAN monomer (mon.) and PAMDAN (pol.) on Pt and GC electrodes.

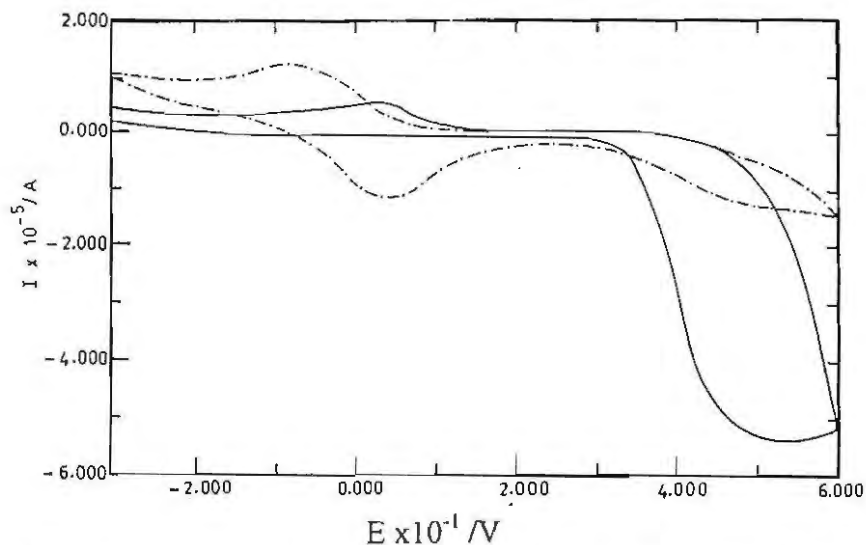| Metal	E_{pa} mon.	E_{pc}. mon.	i_{pa}. mon.	E_{pa}.pol	E_{pc} pol.	i_{pa}. pol	i_{pc}. pol
Pt	0.48 V	0.04 V	$5.5 \times 10^{-5} A/cm^2$	0.05 V	0.09 V	$1.8 \times 10^{-5} A/cm^2$	$0.4 \times 10^{-5} A/cm^2$
GC	0.6 V	0.16 V	$6.8 \times 10^{-5} A/cm^2$	0.20 V	0.16 V	$3 \times 10^{-5} A/cm^2$	$1.5 \times 10^{-5} A/cm^2$

Fig. (2) a: Typical cyclic voltammogram of PAMDAN film formation on Pt electrode in 0.1 M H_2SO_4 solution containing 2×10^{-3} M AMDAN. The electrode potential was sweept repeatedly in the potential range from - 0.2 to 0.8 V at scan rate 0.02 Vs^{-1} after 15 cycles   -) 1st scan, ...) 15th scan.
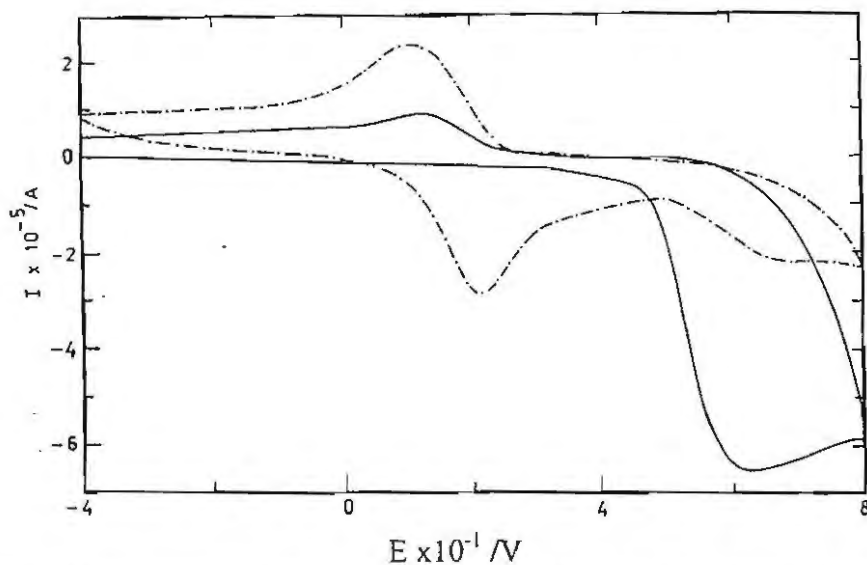

Fig. (2) b: Typical cyclic voltammogram of PAMDAN film formation on GC electrode in 0.1 M H_2SO_4 solution containing 2×10^{-3} M AMDAN. The electrode potential was sweept repeatedly in the potential range from - 0.4 to 0.8 V at scan rate 0.1 Vs^{-1} for 30 cycles -) 1st scan, ...)30th scan.

The data illustrate that the redox potentials (anodic potential E_{pa} and cathodic potential E_{pc} and current densits (anodic peak current i_{pa}, cathodic peak current i_{pc}) for monomer, and polymer are different and depends on electrode substrate. This behavior is though to be due to formation of metal oxide films at the electrode surfaces before the monomer oxidation. The variation in oxidation potentials of AMDAN monomer for the two electrodes may be due to the potential drops across the metal/metal-oxide/ electrolyte interfaces .Two reasons can be proposed for the formation of the metal oxide layers during the cyclic voltammetry (C.V) experiments. The first is that when the micro-electrodes were transferred to the C.V. cell after cleaning, they were in contact with air and an oxide film was formed . The second is that when a C.V. scan was first performed the metal electrode were oxidized and hence passivated before the oxidation potential of the monomer was reached [**Cheung (1988); Biallozor et al., (2005); Laser (1974) and Dai (1996)**]. For these reasons, the nature of the electrode influence the potential peaks and also the current density.

Stabilization of redox process was rapid on Pt electrode (15 cycle were necessary) and slower on GC electrodes (30 cycles were necessary), [**Dai et al., (1996) and Pine et al., (1997)**]. The monomer may be strongly adsorbed on the GC electrode surface. This stabilization of monomer in the adsorbed state may, in turn, diminish the rate of monomeric oxidation to the corresponding radical cation, resulting in slower polymer growth on GC. It is also possible that polymer nuclei form only at defect sites on the oxide-coated GC substrate, and thus few sites are present for subsequent polymer growth [**Lin et al., (1994) and Dinh et al., (2000)**]. The anodic peaks of the monomer are wide than the anodic/cathodic peaks of the polymer this is indicative of a more difficult charge transfer in the case of the monomer than in case of the polymer which indicating the electro active deposited polymer [**Simionescu et al., (1995); Begin et al., (1998); Hathoot (2003) and Meneguzzi et al., (2001)**].

2- Cyclic voltammetrey of PAMDAN modified electrodes.

Pt and GC modified coated with PAMDAN film were washed by distilled water, then dipped in 0.1M H_2SO_4 and scanned in potential range between -0.2 and 0.4 V at different scan rates. The voltammograms (Fig. 3 a,b) show broad peaks for the redox reaction of PAMDAN films. The peak current values and peak redox potentials were effected by the

electrode substrate as shown from fig. 3(a,b). The relation between the potential scan rate (v) and the anodic peak current (i_{pa}) was studied and give a linear relation for Pt and GC modified electrodes, also a linear relation was obtained for the relation between i_{pa} and square root of scan rate ($v^{1/2}$) which give evidence about the charge transport process within the film is diffusion controlled [**Abd El-Rahman et al., (2000); Yonsef et al., (2001); Hathoot (2000); Ismail et al., (2002) and Abd El Azzem et al., (1996)**].

3- Stability and reproducibility of the polymer film.

Much attention should be paid to the stability of chemically modified electrodes [**Abd El-Rahman et al., (2000) and Yousef et al., (2001)**], so the stability of modified Pt and GC electrodes coated by PAMDAN film were tested in 0.1 M H_2SO_4 aqueous solution by scan repetition. The PAMDAN/ GC modified –electrode retained 92% of its initial response after 20 successive potential scans, however in case of PAMDAN/Pt modified electrode about 94% of its initial response was retained under the same condition this indicate that Pt modified electrode has a high stability than GC modified electrode under the same conditions, i.e the electrode substrate influence also the degree of stability of the modified electrode.

4- Electrode catalytic oxidation of hydroquinone at PAMDAN modified electrodes.

PAMDAN modified electrodes have been found to be capable of decreasing the over potential and/or improving the electrochemical reversibility of the redox response of hydroquinone. [**Abd El-Rahman et al., (2000); Yousef et al., (2001); Diab et al., (2000) and Hathoot (2000)**]. Fig.4(a,b) shown the Cyclic voltammograms of 10^{-3} M hydroquinone in 0 .1 M H_2SO_4 recorded at 100 mVs^{-1} on bare and modified electrodes. The result illustrate that the nature of the substrate influence the electro-oxidation process of hydroquinone.
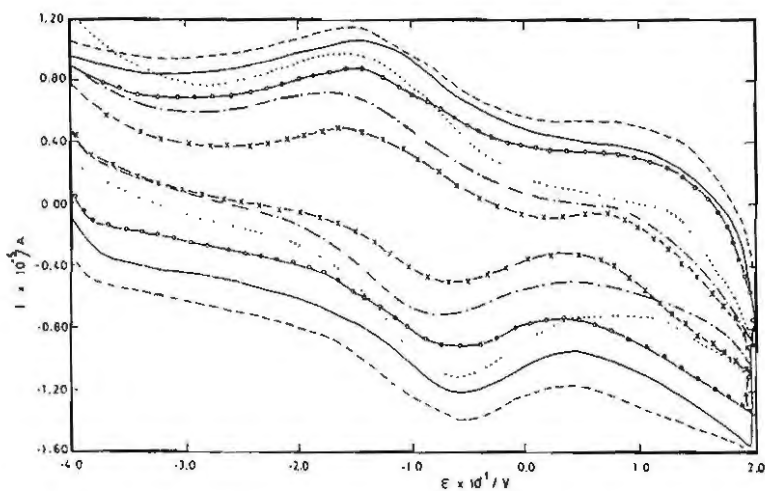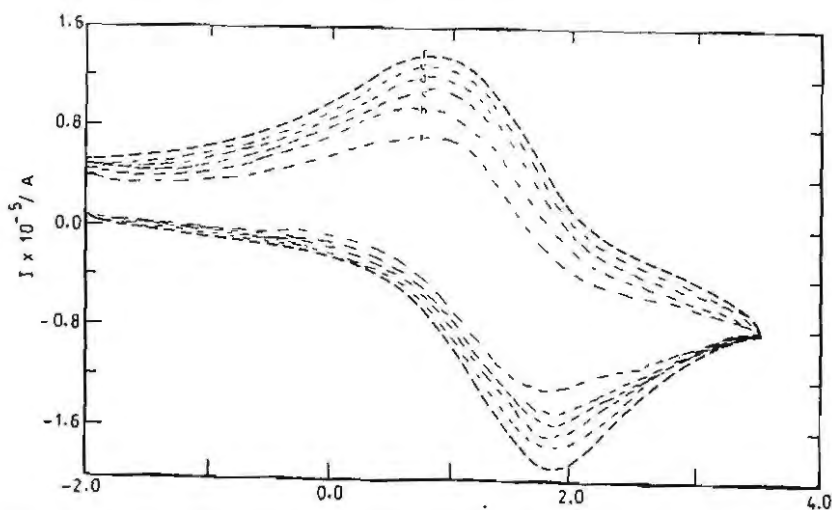
Fig. (3) a: Cyclic voltammetric response of PAMDAN/Pt modified electrode electrode prepared as in fig, 2. a. and tested in 0.1 M H_2SO_4 at different scan rates

x-x) 0.04 Vs^{-1} -. -) 0.06 Vs^{-1} - o -) 0.08 Vs^{-1}
...) 0.1 Vs^{-1} —) 0.12 Vs^{-1} --) 0.14 Vs^{-1}

Fig. (3) b: Cyclic Voltammetric response of P AMDAN/GC modified electrode electrode prepared as in fig, 2. b. and tested in 0.1 M H_2SO_4 at different scan rates

x-a) 0.04 Vs^{-1} b) 0.06 Vs^{-1} c) 0.08 Vs^{-1}
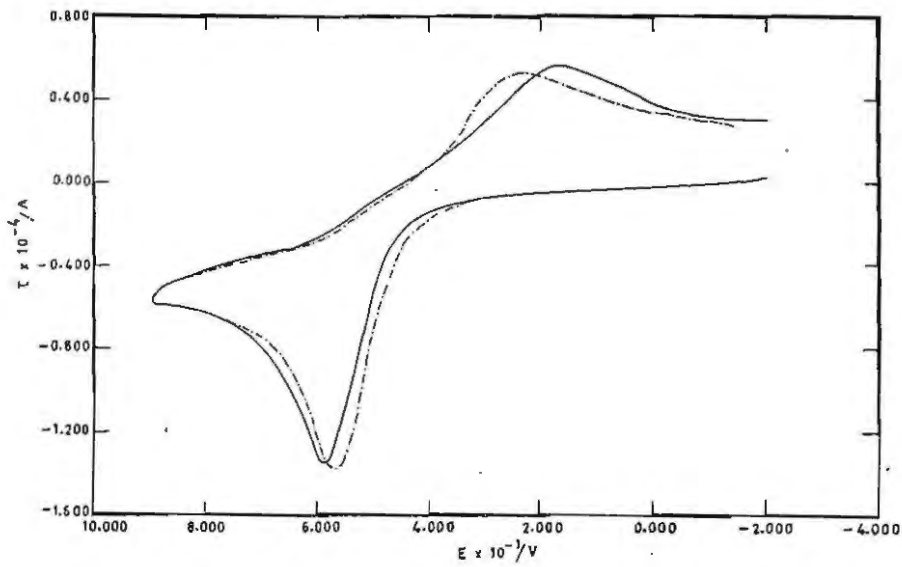d) 0.1 Vs^{-1} e) 0.12 Vs^{-1} f) 0.14 Vs^{-1}

Fig. (4) a: CV for oxidation of 10^{-3} M hydroquinone in 0.1 M H_2SO_4 on (—) bare Pt electrode and (-.-) PAMDAN/Pt modified electrode sweep rate 0.1 Vs^{-1}. the modified electrode was prepared as shown in fig 2. a
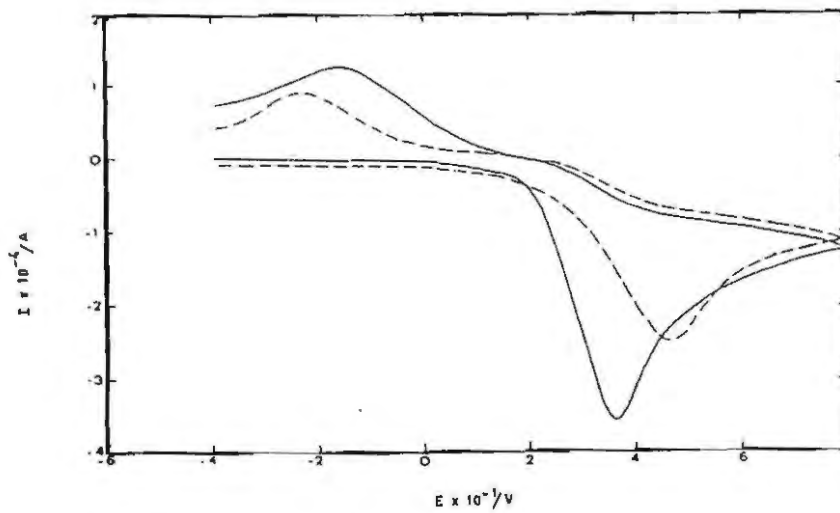

Fig. (4) b: CV for oxidation of 10^{-3} M hydroquinone in 0.1 M H_2SO_4 on (-.-) bare Pt electrode and (—) PAMDAN/GC modified electrode sweep rate 0.1 Vs^{-1}. the modified electrode was prepared as shown in fig 2. b

CONCLUSION

AMDAN monomer can be polymerized in 0.1 M H_2SO_4 by using cyclic voltammetry on Pt and GC electrodes the oxidation potentials of the monomer and the density of voltammetric currents depends, greatly on the nature of the electrode substrate, also the density of voltammetric current depends greatly on the nature of the electrode substrate also the electrochemical response, stability and the electro catalytic behavior of the resulting modified electrode was affected by the nature of the substrate. This behavior may be due to the formation of metal oxide films at the electrode surfaces, and the variation in the oxidation potentials of the monomers for different metal electrodes may be due to the potential drops across the metal/metal-oxide/electrolyte interfaces being different.

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تأثير طبيعة أ لالكترود على البلمرة والخواص الكهربية

لمركب ٨-٣- أستيل أمينو ٦-ميثيل-٢-ثنائى البيران١-أمينو نفتالين

عبلة أحمد حتحوت

استاذ مساعد الكيمياء الفيزيائية بكلية العلوم جامعة المنوفية

هذا البحث يصف التخليق الكهروكيميائى لبولي ٨-٣- أستيل أمينو ٦-ميثيل-٢- ثنائى البيران١-أمينو نفتالين على سطح قطب البلاتين وسطح الكربون الزجاجى فى وسط مائى من حمض الكبريتيك تركيزة ٠,١ مولر وقد وجد أنة يتكون طبقة ثابتة من البوليمر علي سطح كلا القطبين وان جهد التأكسد وشدة التيارللمونيمر يعتمد علي طبيعة القطب المستخدم فى عملية البلمرة. وتم دراسة السلوك الكهربائى للبوليمر فى حمض الكبريتيك ٠,١ مولر عند معدل مسح مختلف ومتعدد. ثبات طبقة البوليمر تمت دراستها بواسطة اعادة الفولتمتر الحلقى المستمر وقد وجد ان البوليمر له سلوك حفزى وان هذا السلوك يعتمد على طبيعة الالكترود المستخدم وهذا يرجع الى تكوين طبقة رقيقة من الاكسيد على سطح القطب قبل تكوين البوليمر وانخفاض فى الجهد بين سطح القطب وطبقة الاكسيد والالكتروليت الفاصل.