



Electrochemical Investigation of Poly Furfuryl alcohol (PFA) Doped with Crystal Violet

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ABSTRACT

The electrochemical behavior was investigated of poly Furfuryl alcohol (PFA) by using the cyclic voltammetry technique. Such investigation mainly focuses on the expected properties of the doped polymers with different doping ratios of crystal violet (0.01, 0.03, 0.05, 0.07, 0.1) %wt. This is indicated by the electron transfer between the dopants and both polymers, which clearly shows the appearance of oxidation – reduction peaks accompanied log increase in electrical current I_p as applied potential changes. The heights of I_p oscillate due to the change in scan rate, v . The results of linear of relationships between I_p with $v^{1/2}$ indicated that the electron transfer was a process of one electron transfer.

Keywords: Cyclic voltammetry, poly Furfuryl alcohol, crystal violet, supporting electrolyte.

INTRODUCTION

Cyclic voltammetry is a very important electrochemical technique. It can be used to study the redox behavior of compounds and probe coupled chemical reactions, in particular to determine mechanisms and rates of oxidation/reduction reactions.

The study of cyclic voltammetry with different scan rates offers much information about electron transfer, kinetics and transport properties of electrolysis reaction. The current is measured as a function of the linear potential applied. Such current variation that results when the electrode potential is varied can provide valuable insight into the reactions that occur at the electrode surface [1].

The cyclic voltammetry (scanning in forward and back directions) and linear voltammetry (scanning in one direction) are the most widely used techniques to investigate electrode reaction mechanisms. They are easy to apply experimentally, readily available in commercial instruments and provide a wealth of mechanistic information. In such experiments, the potential of the working electrode is controlled by a potential ramp or one or more potential triangle.

The peak current in a cyclic voltammogram containing only one species is described by Sevcik- Randles[2]:

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C^* \quad (1)$$

at 25 °C where I_p is the peak current, n is the number of electrons transferred, A is the electrode area, D is the diffusion coefficient of the species, v is the scan rate and C^* is the bulk concentration of the species. If the diffusion constants for the oxidized and reduced species are similar, the value of E^0 (formal potential) can be estimated from

the average of E_{pa} and E_{pc} , where E_{pa} is the potential of the anodic peak current and E_{pc} is the potential of the cathodic current[3].

Cyclic voltammetry is a useful technique for probing the processes that occur at the electrode/solution interface. This technique is not generally well understood in comparison to other instrumental methods such as spectroscopy and chromatography. It is not uncommon for the experimenter who is performing CV to have a poor understanding of the basic concepts of the technique, such as why the voltammograms have their peculiar shapes [4].

MATERIALS AND METHODS

2.1 Materials

The materials tested in this study were Furfuryl alcohol, dimethyl formamide, Sulfuric acid, crystal violet and Tetrabutylammoniumtetrafluoroborate.

2.2 Preparation of poly Furfuryl alcohol (PFA)

PFA has been prepared from the distilled liquid monomer FA (25 ml) via drops of acid catalysis H_2SO_4 (1M) and heated at $60^\circ C$ for 1 hour to yield viscose colored polymer [5-8].

2.3 Doping of PFA

Doping PFA with dye crystal violet is carried out by adding the weighed dye to the appropriate weight of polymer (1g) then the mixture was dissolved in dimethyl formamide DMF after the prepared directly to give a polymer / dye system containing (0.01, 0.03, 0.05, 0.07 and 0.1) g wt% of doping reagent Crystal violet [9]. The mixture was stirred well for 15 minutes to guarantee that the homogenous distribution of dye in the polymer matrix.

2.4 Electrochemical measurements

Cyclic-Voltammetry (CV) was carried out in a thermostated one compartment three –electrode cell. The working electrode was a platinum wire of nominal area 0.0785 cm^2 . This was controlled by silver-silver chloride as a reference electrode through which no current flows. The auxiliary (secondary) electrode was a platinum wire. Cyclic voltammetry was performed with a DY 2300 Series Potentiostat /Bipotentiostat, potentiostate-galvanostate fully computerized in the processed data analysis.

In cyclic voltammetry (CV), the voltage is linearly varied from initial to final potential values as required and then directly swept back at the same sweep rate to the initial one. The current response is plotted as a function of voltage rather than time . The species were reduced and oxidized in the manner of reversible reactions. During all measurements Bu_4NBF_4 was used as a supporting electrolyte.

In cyclic voltammetry, the negative initial potential value was set mostly equal to the final positive one. The scan rate (v) was varied from 0.1 to 1 Vs^{-1} , while the voltage was scanned between -2 to 2V. The molar concentration of supporting electrolyte Bu_4NBF_4 was 0.15 M. The solutions of pure PFA as well as the doped solutions with different weight ratios of crystal violet (0.01, 0.03, 0.05, 0.07, 0.1) wt% were all subjected to cyclic voltammogram, in order to achieve a comparison with the measured precursor cyclic voltammograms of pure solutions. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

The electrochemical behavior of the PFA and its doping ratios were established by cyclic voltammetry (CV) for oxidation and reduction at a platinum electrode in DMF at scan rates that ranged from 0.1 to 1 Vs^{-1} at a potential range of 2 to -2V. At scan rate (v) 0.1 Vs^{-1} , as an example, two reduction peaks were clearly obtained for PFA. The first reduction peak is obtained at $E_{pred1} = -0.375\text{V}$ corresponding to the cathodic peak current $I_{pred1} = 1.5 \times 10^{-5}\text{A}$. The second peak is located $E_{pred2} = -0.75\text{V}$ corresponding to the cathodic peak current $I_{pred2} = 1.6 \times 10^{-5}\text{A}$, as shown in Figure (1).

It is obvious that the reduction peaks were shifted to more negative potential values as v increases accompanied by an increase in the current peak. This behavior is indicated and confirmed by Sevcik-Randles equation (1).

According to the same Equation (1), given in chapter one, which has given the relationship between the peak current I_p and the square root of the scan rate $v^{1/2}$, the following graphic relations are established

$$\begin{aligned} I_p &\propto v^{1/2} \\ F_p &\propto v \end{aligned}$$

Where $F_p = I_p / v^{1/2}$ and is known as current function. So, both F_p^{red} (reduction) and F_p^{ox} (oxidation) can be computed. Table (1) illustrates the obtained data for the two reduction states of the PFA, and Figure (2) represents a linear relationship between $I_{p_{red}}$ with $v^{1/2}$ of PFA indicating that the electron transfer is a process of one electron transfer. Figure (3) shows the plot of F_p versus v from which it is clear that the F_p is essentially invariant with v provided that $v > 0.1 \text{ Vs}^{-1}$ a condition which isolates the primary electron transfer from the subsequent chemical step. The independence of F_p is a diagnostic signal of diffusion-controlled electron transfer at specified potentials beyond the peak potential [10,11].

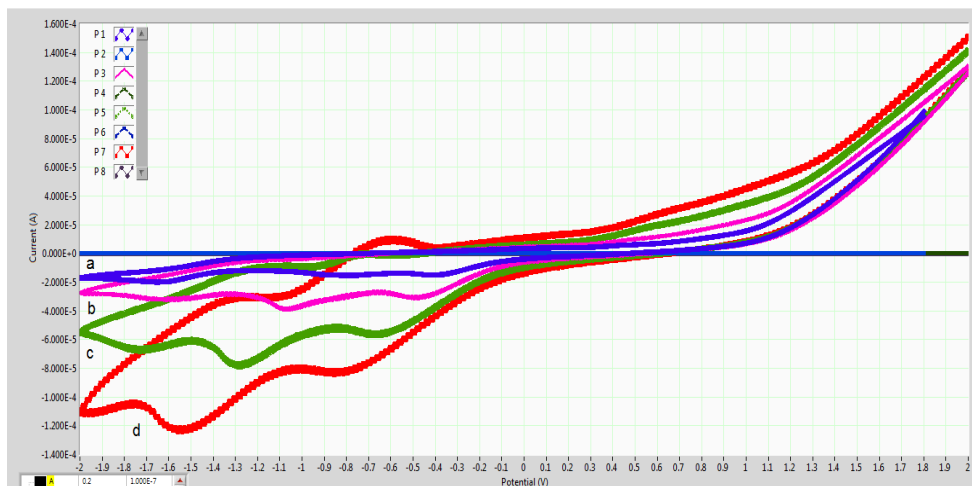


Figure (1):Cyclic voltammogram for PFA at scan rates (a) 0.1Vs⁻¹ (b) 0.2 Vs⁻¹ (c) 0.5 Vs⁻¹ (d) 1 Vs⁻¹

Table(1): Cyclic Voltammogram data of PFA at different scan rates

$v \text{ V.sec}^{-1}$	$\sqrt{v} \text{ (Vs}^{-1}\text{)}^{1/2}$	$I_{p_{red1}} \text{ A (10}^{-5}\text{)}$	$F_p^{red1} \text{ A/(V.s}^{-1}\text{)}^{1/2} \text{ (10}^{-5}\text{)}$	$I_{p_{red2}} \text{ A (10}^{-5}\text{)}$	$F_p^{red2} \text{ A/(V.s}^{-1}\text{)}^{1/2} \text{ (10}^{-5}\text{)}$
0.1	0.316	1.6	5.06	1.5	4.74
0.2	0.447	3.3	7.38	4	8.94
0.5	0.707	6	8.4	8	11
1	1	8.8	8.8	12.5	12.5

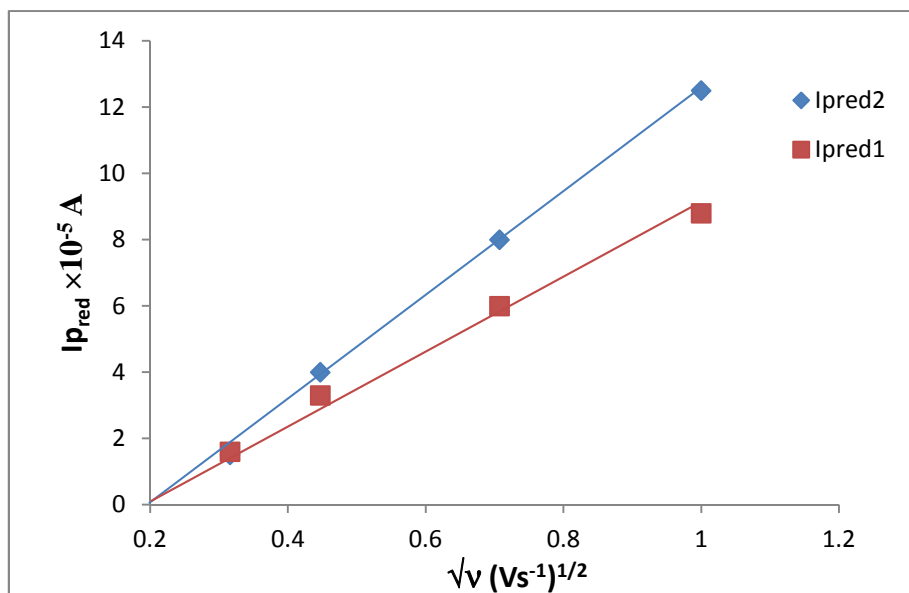


Figure (2): $I_{p_{red1}}$ and $I_{p_{red2}}$ peaks of reduction versus $v^{1/2}$ for PFA

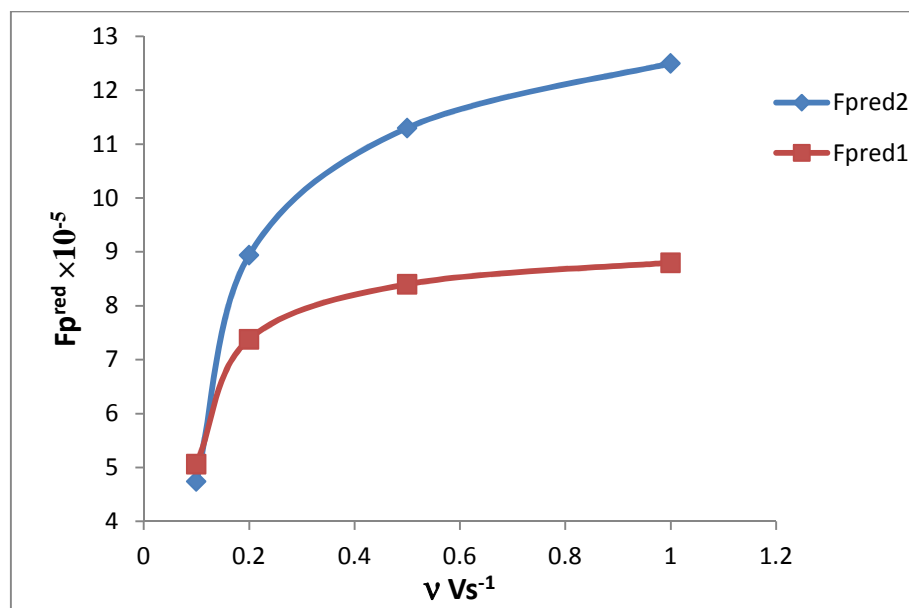


Figure (3): Current function $F_{\text{pred}1}$ and $F_{\text{pred}2}$ versus scan rate for PFA

Upon doping PFA with the dye crystal violet, one of the cathodic peaks disappeared while two oxidation peaks appeared at the same time for all doping ratios. It was noticed that the peaks increase in current values as the doping ratios increase. This is probably due to the transfer of electrons from the valence band to the conduction band which causes current growth in value as v increase [12].

Figure (4) shows the cyclic voltammogram of (0.01%) doping of PFA at a potential range of 2 to -2V at different scan rates. At scan rate 0.1 Vs^{-1} the ratio exhibited two oxidation peaks, the first oxidation peak appeared at $E_{\text{pox}} = 0.35\text{V}$ corresponding to anodic peak current $I_{\text{pox}1} = 2 \times 10^{-5} \text{ A}$, while the second peak $E_{\text{pox}2} = 0.9\text{V}$ corresponding to the anodic peak current $I_{\text{pox}2} = 4.8 \times 10^{-5} \text{ A}$. At the same scan rate and potential range, the cyclic voltammogram shows also a reduction peak at $E_{\text{pred}} = -1.02\text{V}$ with peak cathodic current $I_{\text{pred}} = 4 \times 10^{-5} \text{ A}$, and at scan rate 0.2 Vs^{-1} , 0.5 Vs^{-1} and 1 Vs^{-1} a new oxidation peak observed at $E_{\text{pox}} = -0.625\text{V}$ with anodic peak current $I_{\text{pox}} = 1 \times 10^{-5} \text{ A}$ shifted to higher values as v increases. It is obvious that the oxidation potential peaks are shifted to more positive values as v increases.

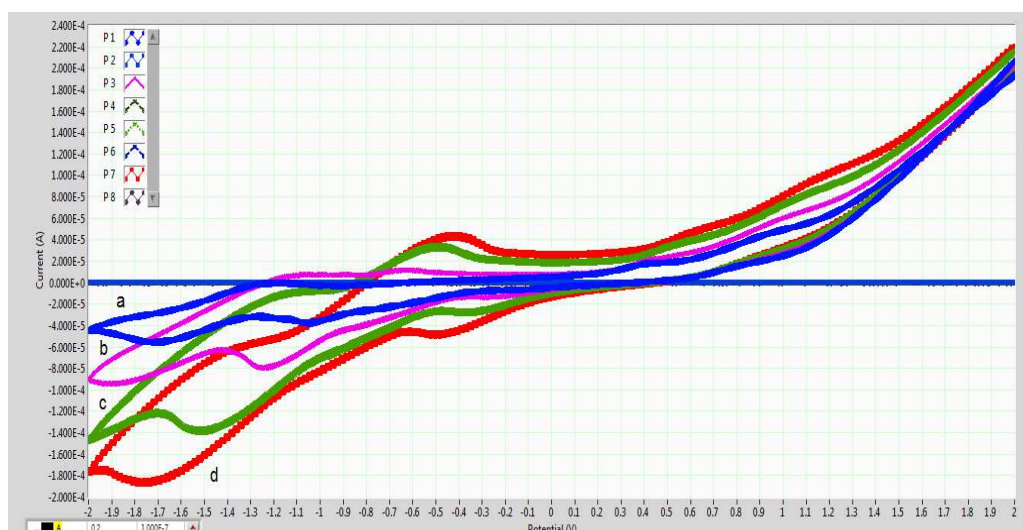


Figure (4): Cyclic voltammogram for 0.01% doping of PFA at scan rates (a) 0.1 Vs^{-1} (b) 0.2 Vs^{-1} (c) 0.5 Vs^{-1} (d) 1 Vs^{-1}

The results are given in table (2). A linear relationship was obtained between I_p and $v^{1/2}$ indicating one electron transfer [13] as shown in figure (5), while figure (6) shows the relationship between F_{pox} versus v indicating the same condition Figure (3) of isolation between the primary electron transfer and that of subsequent chemical step.

Table(2): Cyclic Voltammogram data of 0.01% doping of PFA at different scan rates

v V.sec ⁻¹	\sqrt{v} (Vs ⁻¹) ^{1/2}	$I_{p_{red1}}$ A (10 ⁻⁵)	Fp_{red1} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)	$I_{p_{ox1}}$ A (10 ⁻⁵)	Fp_{ox1} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)	$I_{p_{ox2}}$ A (10 ⁻⁵)	Fp_{ox2} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)
0.1	0.316	4	12.65	2	6.32	4.8	15.18
0.2	0.447	8.4	18.79	2.6	5.81	6	13.42
0.5	0.707	14	19.8	3.9	5.5	8.1	11.45
1	1	19	19	5.2	5.2	11	11

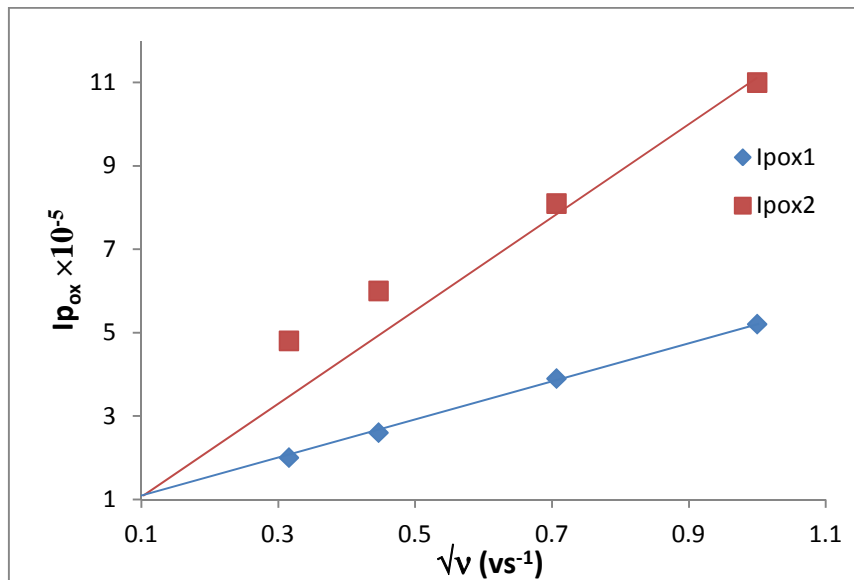


Figure (5): $I_{p_{ox1}}$ and $I_{p_{ox2}}$ peaks of oxidation versus $v^{1/2}$ for 0.01% doping of PFA

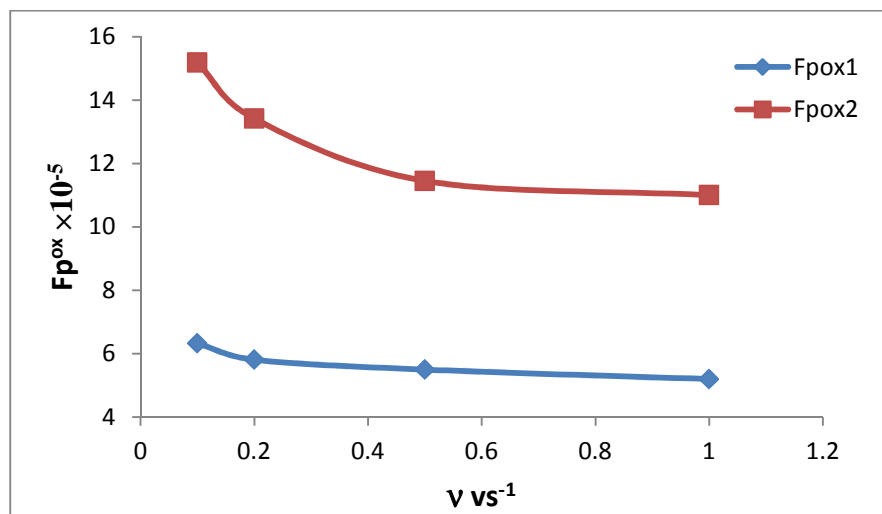


Figure (6): Current function $F_{p_{ox1}}$ and $F_{p_{ox2}}$ versus scan rate for 0.01% doping of PFA

The cyclic voltammogram of (0.03%) doping of PFA in DMF at scan rate 0.1 Vs⁻¹ and potential range from 2 to -2 Figure (7), shows two oxidation peaks at $E_{p_{ox1}}=0.43$ v and $E_{p_{ox2}}=0.93$ v with peak oxidation current $I_{p_{ox1}} = 2.8 \times 10^{-5}$ A and $I_{p_{ox2}} = 5.5 \times 10^{-5}$ A respectively . Also a reduction peak at $E_{red}=-1.04$ v with peak reduction current $I_{red} = 2.6 \times 10^{-5}$ A was indicated.

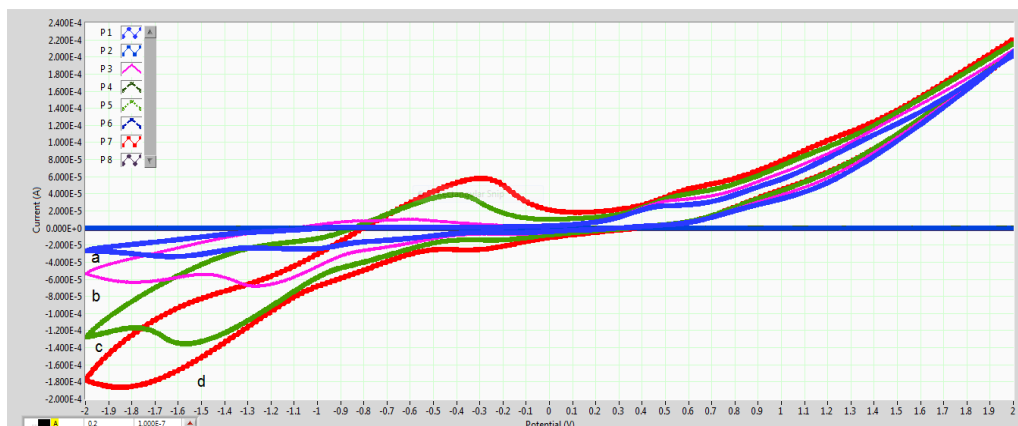


Figure (7):Cyclic voltammogram for 0.03% doping of PFA at scan rates (a) 0.1Vs⁻¹ (b) 0.2 Vs⁻¹ (c) 0.5 Vs⁻¹ (d) 1 Vs⁻¹

As before, the same trend was obtained at other scan rates, 0.2V⁻¹, 0.5V⁻¹ and 1Vs⁻¹ a new oxidation peak observed at E_{pox} = -0.6v with anodic peak current I_{pox} = 1.2 x 10⁻⁵A. The oxidation peaks potential are shifted to more positive values as v increases, while the reduction peak shifted to higher negative values, as shown in figure (7).

The corresponding results were summarized in Table (3), again a linear relationships between both I_{pred} and I_{pox} with v^{1/2} were detected, that the electron transfer is a process of one electron as shown in figure (8), while figure (9) shows the relationships between F_p with v for both oxidation and reduction conforming the same characteristics as mentioned before for 0.01%.

Table(3): Cyclic Voltammogram data of 0.03% doping of PFA at different scan rates

v V.sec ⁻¹	\sqrt{v} (Vs ⁻¹) ^{1/2}	I _{pred1} A (10 ⁻⁵)	F _{p^{red1}} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)	I _{pox1} A (10 ⁻⁵)	F _{p^{ox1}} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)	I _{pox2} A (10 ⁻⁵)	F _{p^{ox2}} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)
0.1	0.316	2.6	8.22	2.8	8.8	5.5	17.4
0.2	0.447	7	15.6	3.2	7.15	7	15.6
0.5	0.707	13.8	19.5	4	5.65	8.8	12.44
1	1	19.2	19.2	4.8	4.8	12	12

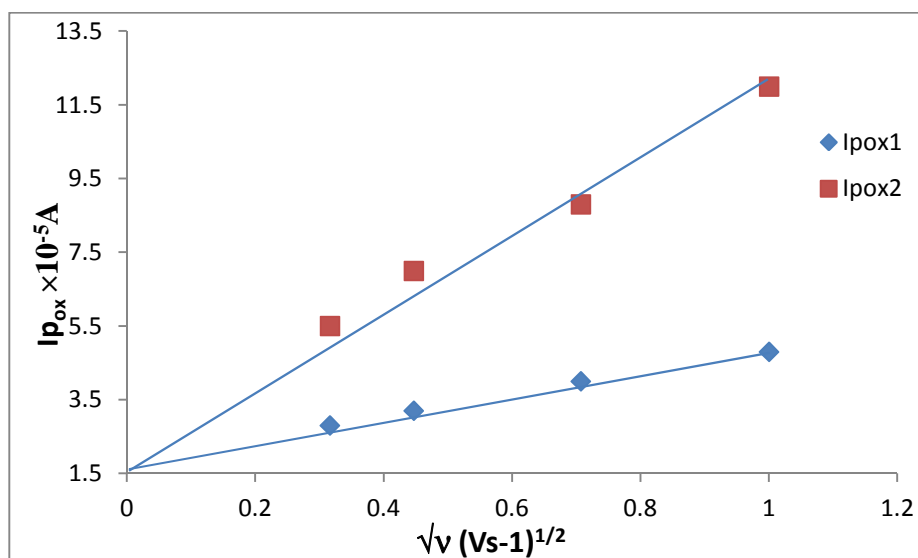


Figure (8):Ip_{ox1} and Ip_{ox2} peaks of oxidation versus v^{1/2} for 0.03% doping of PFA

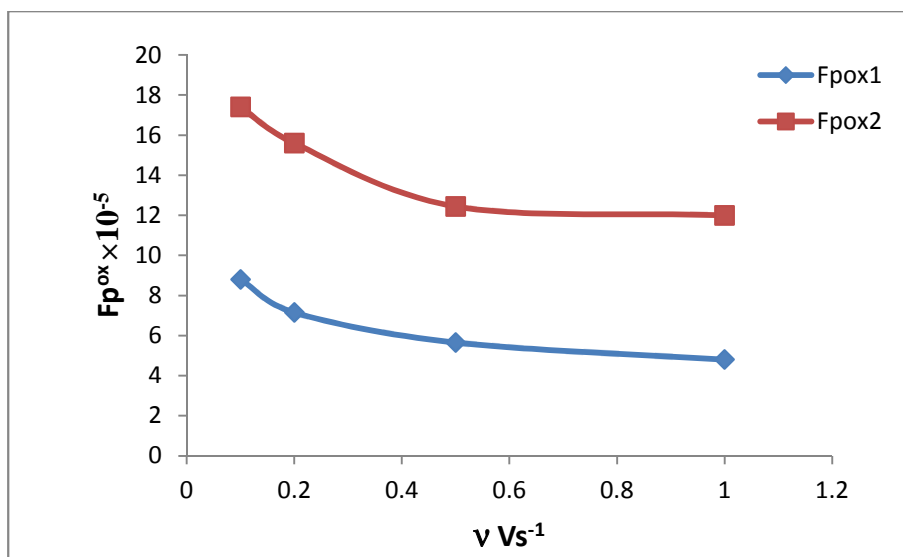


Figure (9): Current function Fp^{ox1} and Fp^{ox2} versus scan rate for 0.03% doping of PFA

Figure (10) shows the cyclic voltammogram of (0.05%) doping of PFA at a potential range of 2 to -2v at different scan rates, while the results of all cyclic voltammogram data are collected in table (4). It is concluded that as percentage of doping increases the resultant currents increase gradually indicating more electron transfer occurrence.

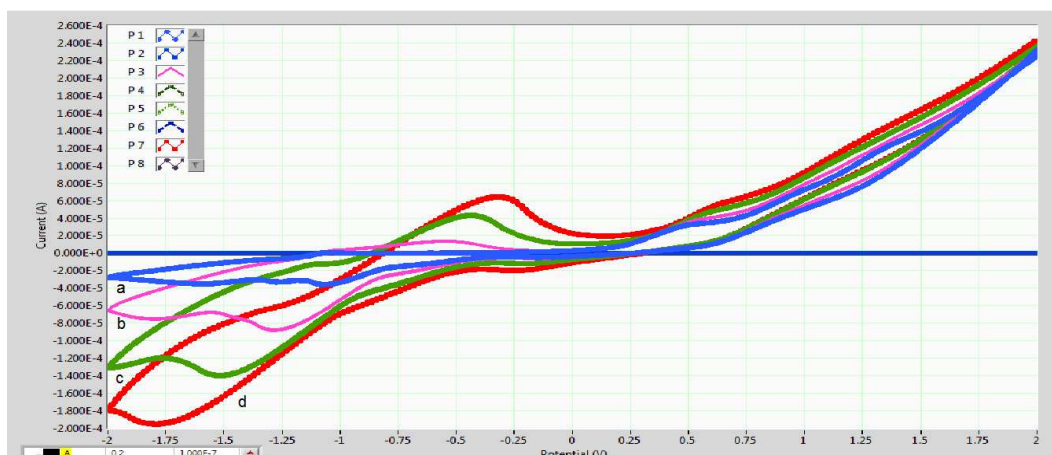


Figure (10):Cyclic voltammogram for 0.05% doping of PFA at scan rates (a) 0.1Vs⁻¹ (b) 0.2 Vs⁻¹ (c) 0.5 Vs⁻¹ (d) 1 Vs⁻¹

As examples, Figure (11) illustrate once more a linear relationships for oxidation processes giving rise to one electron transfer as well its before the same trend was exhibited in Figure (12).

Table(4): Cyclic Voltammogram data of 0.05% doping of PFA at different scan rates

v $V.sec^{-1}$	\sqrt{v} $(Vs^{-1})^{1/2}$	$I_{p_{red1}}$ A (10^{-5})	Fp^{red1} A/($V.s^{-1}$) ^{1/2} (10^{-5})	$I_{p_{ox1}}$ A (10^{-5})	Fp^{ox1} A/($V.s^{-1}$) ^{1/2} (10^{-5})	$I_{p_{ox2}}$ A (10^{-4})	Fp^{ox2} A/($V.s^{-1}$) ^{1/2} (10^{-4})
0.1	0.316	3.8	12	3.5	11.07	0.92	2.91
0.2	0.447	9	20.13	3.9	8.72	1	2.23
0.5	0.707	14.2	20.08	4.7	6.64	1.2	1.69
1	1	19.8	19.8	5.5	5.5	1.42	1.42

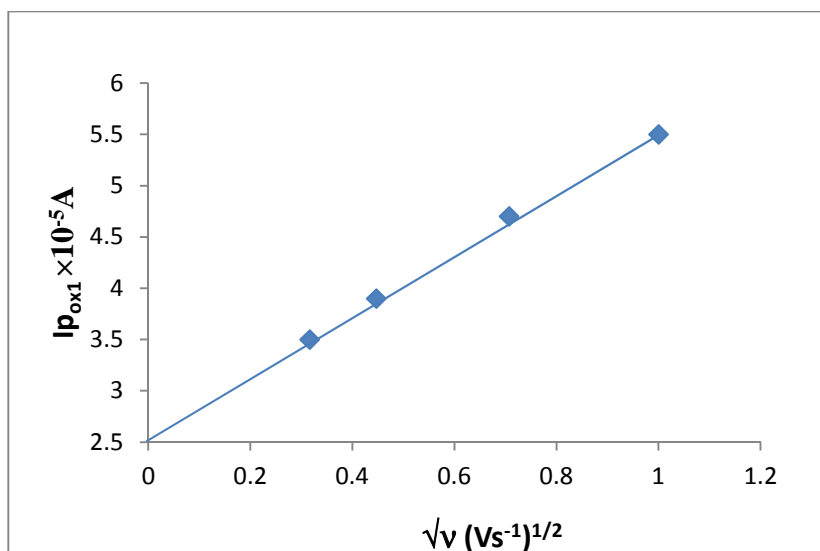


Figure (11): $I_{p_{ox1}}$ peak of oxidation versus $v^{1/2}$ for 0.05% doping of PFA

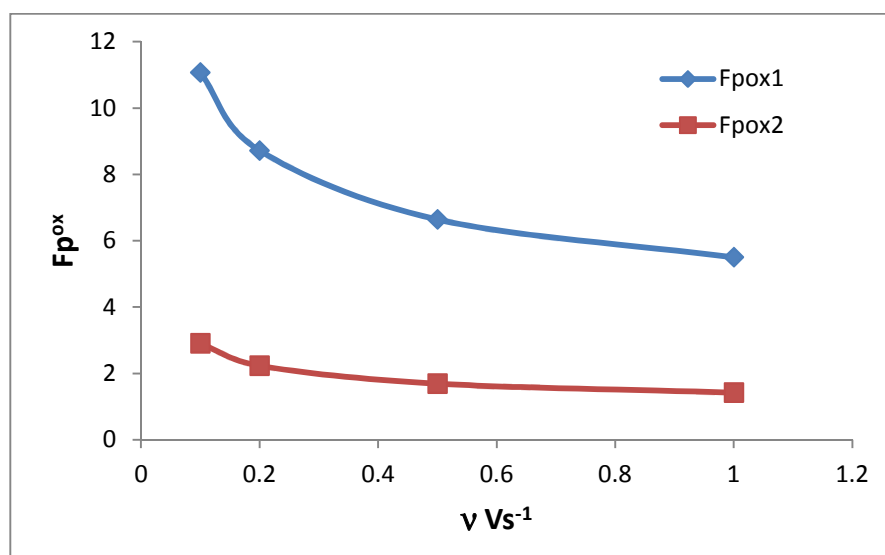


Figure (12): Current function $F_{p_{ox1}}$ and $F_{p_{ox2}}$ versus scan rate for 0.05% doping of PFA

In comparison with the preceding percentage, the cyclic voltammogram of (0.07%) doping of PFA in DMF at scan rate 0.1 Vs^{-1} and potential range from 2 to -2V shows two oxidation peaks at $E_{p_{ox1}}=0.48\text{V}$ and $E_{p_{ox2}}=1.2\text{V}$ with peak oxidation current $I_{p_{ox1}} = 4.1 \times 10^{-5}\text{A}$ and $I_{p_{ox2}} = 1.14 \times 10^{-4}\text{A}$ respectively as shown in Figure (13). Also, the cyclic voltammogram shows reduction peaks at $E_{p_{red1}} = -1.18\text{V}$ with cathodic peak current $I_{p_{red}} = 3.7 \times 10^{-5}\text{A}$. The oxidation peaks are shifted to more positive values, while the reduction peak shifted to higher negative values as v increases. This is obvious from Figure. The main oxidation and reduction peaks increased linearly as the scan rate was increased from 0.1 to 1 Vs^{-1} indicating more electron transfer on doping. Table (5) illustrates the results of all cyclic voltammogram data of 0.07% doping of PFA.

Figure (14) shows the specific relations between $I_{p_{red}}$ and $I_{p_{ox}}$ with $v^{1/2}$ characterized linear relationships, which indicate one electron transfer under a controlled diffusion process. Figure (15) shows the same trend as other preceding percentages between $F_{p_{ox}}$ with v .

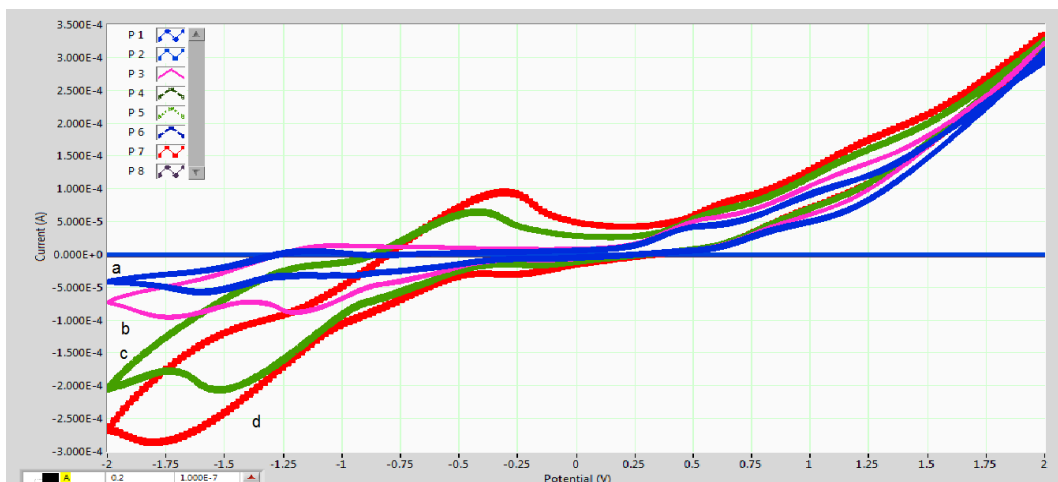


Figure (13):Cyclic voltammogram for 0.07% doping of PFA at scan rates (a) 0.1Vs⁻¹ (b) 0.2 Vs⁻¹ (c) 0.5 Vs⁻¹ (d) 1 Vs⁻¹

Table(5): Cyclic Voltammogram data of 0.07% doping of PFA at different scan rates

v V.sec ⁻¹	\sqrt{v} (Vs ⁻¹) ^{1/2}	I _{p_{red1}} A (10 ⁻⁵)	F _{p_{red1}} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)	I _{p_{ox1}} A (10 ⁻⁵)	F _{p_{ox1}} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)	I _{p_{ox2}} A (10 ⁻⁴)	F _{p_{ox2}} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁴)
0.1	0.316	3.7	11.7	4.1	12.97	1.14	3.6
0.2	0.447	9.2	20.58	5.5	12.3	1.31	2.93
0.5	0.707	21.2	29.98	5.8	8.2	1.58	2.23
1	1	29	29	8	8	1.9	1.9

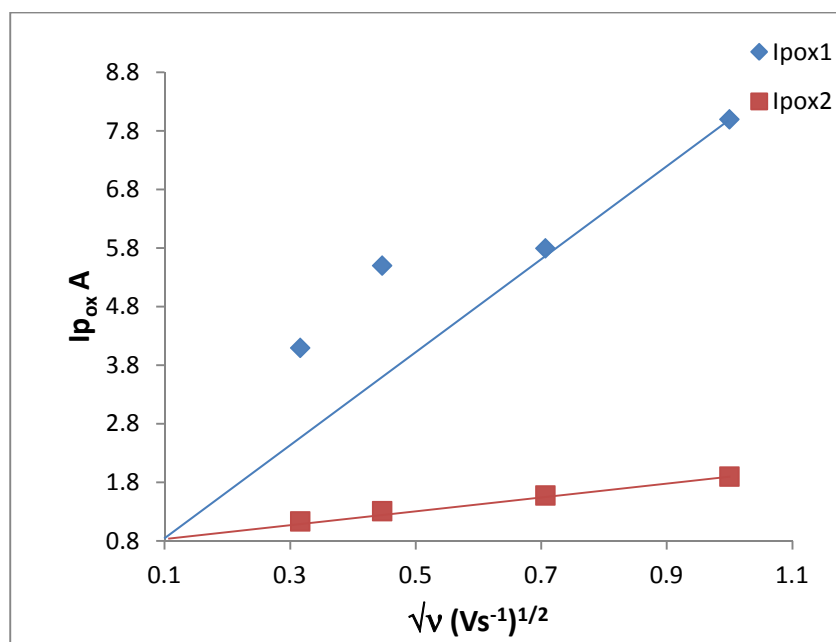


Figure (14):Ip_{ox1} and Ip_{ox2} peaks of oxidation versus v^{1/2} for 0.07% doping of PFA

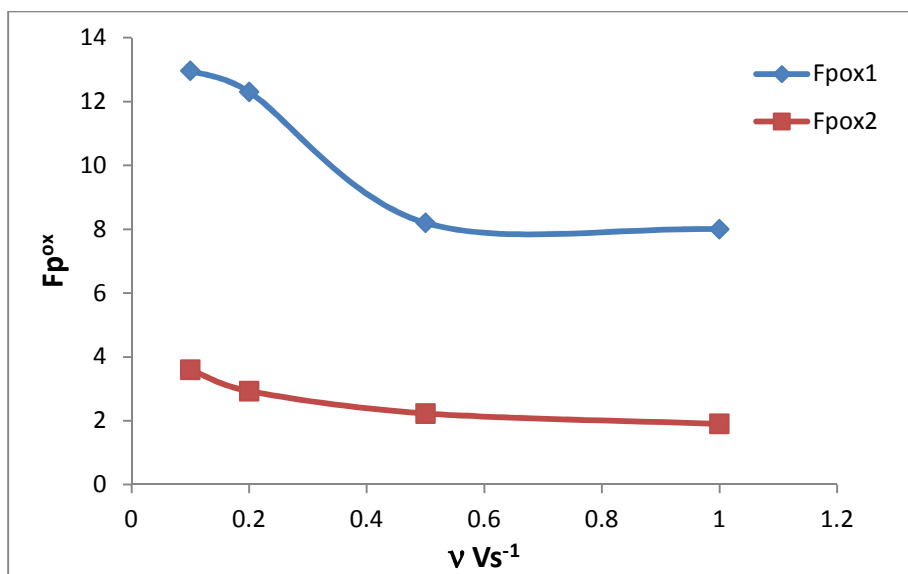


Figure (15): Current function Fp^{ox1} and Fp^{ox2} versus scan rate for 0.07% doping of PFA

The cyclic voltammogram of last percentage (0.1%) doping of PFA at a potential range of 2 to -2V at different scan rates show the same behavior as given before, which is abbreviated in Figure (16). All related results are written down in Table (6). Figure (17) shows linear relations between $I_{p_{ox}}$ with $v^{1/2}$ which indicate once more one electron transfer under a controlled diffusion process, while Figure (18) shows the relations between Fp^{ox} with v .

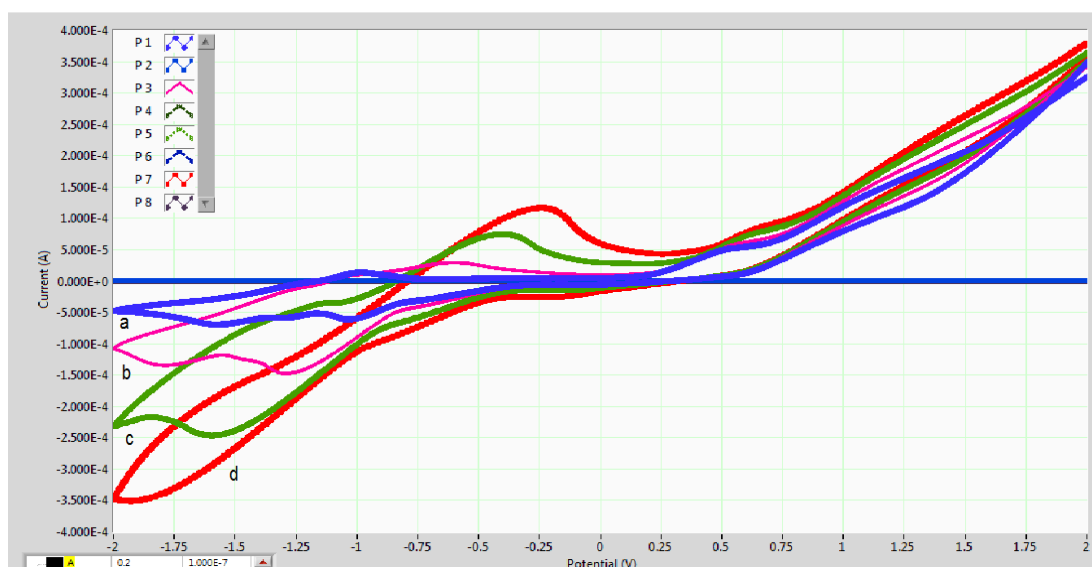


Figure (16):Cyclic voltammogram for 0.1% doping of PFA at scan rates (a) 0.1Vs⁻¹ (b) 0.2 Vs⁻¹ (c) 0.5 Vs⁻¹ (d) 1 Vs⁻¹

Table(6): Cyclic Voltammograms data of 0.1% doping of PFA at different scan rates

v V.sec ⁻¹	\sqrt{v} (Vs ⁻¹) ^{1/2}	$I_{p_{red1}}$ A (10 ⁻⁴)	Fp^{red1} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁴)	$I_{p_{ox1}}$ A (10 ⁻⁵)	Fp^{ox1} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁵)	$I_{p_{ox2}}$ A (10 ⁻⁴)	Fp^{ox2} A/(V.s ⁻¹) ^{1/2} (10 ⁻⁴)
0.1	0.316	0.63	1.99	5	15.82	1.6	5.06
0.2	0.447	1.5	3.35	6	13.42	1.8	4.02
0.5	0.707	2.5	3.53	7	9.9	2.25	3.18
1	1	----	----	9.2	9.2	2.7	2.7

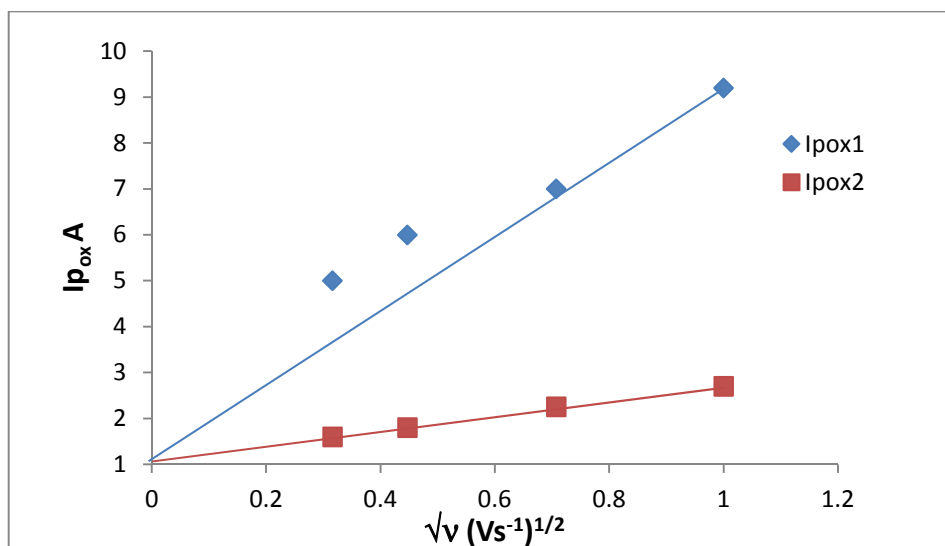


Figure (17): $I_{p_{ox1}}$ and $I_{p_{ox2}}$ peaks of oxidation versus $v^{1/2}$ for 0.1% doping of PFA

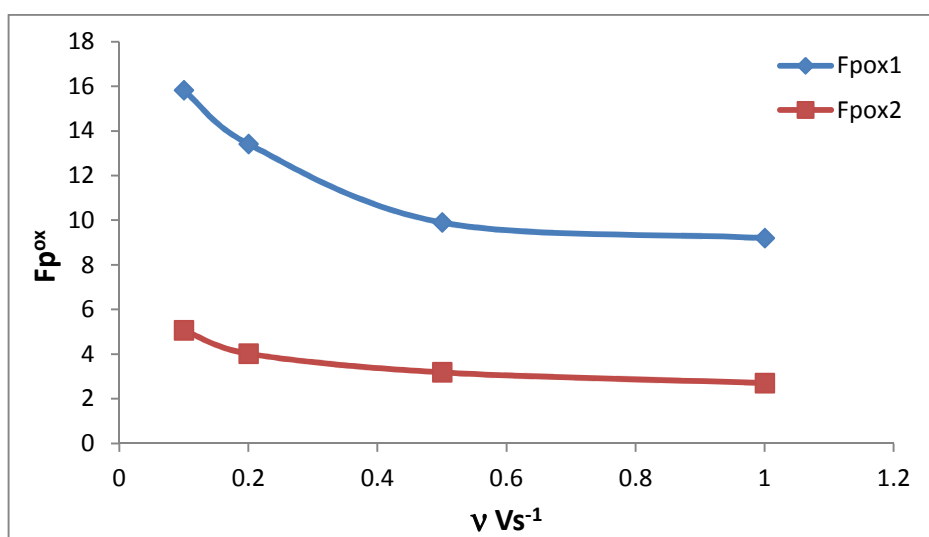


Figure (18): Current function $F_{p_{ox1}}$ and $F_{p_{ox2}}$ versus scan rate for 0.1% doping of PFA

Upon comparison, the effect of the different percentages that have been used, it is concluded that 0.07% is the best one among others. Bulk conductivity in doped polymer material is limited by the need for the electrons to jump from one chain to the next, i.e., in molecular terms an intermolecular charge transfer reaction. It is also limited by macroscopic factors such as bad contacts between different crystalline domains in the material [14].

CONCLUSION

In the study of cyclic voltammetry, the results of linear relationship between $I_{p_{red}}$ with $v^{1/2}$ of all doped poly furfuryl alcohol (PFA) with different ratios of crystal violet that the electron transfer was a process of one electron transfer.

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