

Electrochemical Behavior and Characterization of Grafted Polystyrene-Acrylonitrile Electrodes

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The redox of grafted polymer electrodes GPE (grafted polystyrene-acrylonitrile, GP15%, GP45% and GP50% grafting percentage) in aqueous electrolyte has been studied under various voltammetric conditions. In this work, voltammetric studies were carried out, principally in electrolyte containing potassium chloride. It was observed that GP15% has a good potential window at -2.0 - +2.0V without any current peak, while GP45% has reduction and oxidation current peaks at -175.9 and +210mV respectively. Also GP50% has oxidation and reduction current peaks at +263.1 and -261.9mV respectively. The redox process is irreversible in aqueous electrolyte containing different alkaline cations, such as Na⁺, K⁺, Rb⁺ and Cs⁺. The shift of redox potential was found to follow the change in the hydration energy in the order: Cs⁺ > Rb⁺ > K⁺ > Na⁺. In addition, the redox peaks of the fabricated electrodes from GP were also studied in aqueous electrolytes at different anions (KCl, KClO₄, K₂HPO₄, KNO₃ and K₂SO₄), which gave good redox peaks in KCl and enhanced the redox current via increasing the concentration. Electrochemical experiments reveal that the grafted polymer electrodes show improved electron-transfer characteristics and exhibit high electrocatalytic activity for grafted percentage in the order of : 15% > 45% > 50%. The applications of these electrodes, especially type 15%, are in the cyclic voltammetric technique when used as a working electrode.

Keywords: Grafted Polymer Electrode, Cyclic Voltammetry, Electrocatalyst, KCl electrolyte

1. INTRODUCTION

Working electrodes act as a source or sink of electrons for exchange with molecules in the interfacial region. They must be an electronic conductor and electrochemically inert. Commonly used working solid electrode materials for cyclic voltammetry include platinum, gold and glassy carbon. Other materials (e.g., semi-conductors, for example ITO, indium-tin oxide, or conductive polymers or

grafted polymer) are also used, for more specific applications. Polystyrene is a polymer made from the monomer styrene. At room temperature, polystyrene is normally a solid thermoplastic, colorless and harder plastic. It has low thermal conductivity of 0.08 W/m.k. and an electrical conductivity (σ) of 10^{-16} S m⁻¹. A copolymer of acrylonitrile and styrene, are toughened with polybutadiene. Conductive polymers are good candidates for preparation of conducting grafted copolymers [1,2]. Many types of conducting polymers had been synthesized at recent times, the polymers that were reported largely focused on polyacetylene, polyaniline, polyfuran, polythiophene, polypyrrole and their functional derivatives, whilst relatively lesser work was conducted on polyselenophene [3,4]. A new conducting copolymer, polyacrylonitrile-graft-polyaniline, has been prepared by chemical and electrochemical methods from a precursor polymer. Electrical conductivity of the copolymer was studied using the four-probe method, which gave a conductivity of 4.5×10^{-3} S cm⁻¹ with 51.4% polyaniline [5].

Electroactive polymers possess groups susceptible to electron transfer reactions at electrodes. For reversible electron transfer, the polymers are classified as electron-transfer or redox polymers or copolymers [6-8]. Studies of the behavior of electroactive redox groups incorporated into macromolecular structures or polymer systems are of both theoretical and practical importance. The principle of solid-state electrode devices is based on their electrical response to the chemical solution. Such a change in electrical properties is used to detect the chemical species. Solid-state electrodes have been made not only from classical metals like Au, Pt, GC electrodes, but also from polymers, copolymers or semiconductors which have good reproducibility, stability, sensitivity and selectivity [9,10]. Grafted copolymers were prepared by copolymerization of acrylonitrile with poly(sodium styrene sulfonate). This grafted copolymer has the effect of lowering proton conductivity, due to dilution of ions; increasing the diffusion coefficient of oxygen; and decreasing the oxygen solubility in the membrane [11]. Grafted polystyrene with acrylonitrile was prepared as a thin film on glass substrate using spray technique. It was found that the conductivity decreases upon increasing grafting percentage. The ionic jump distances values and the variation of ionic jump distance with grafting percentage were calculated [12]. Electrochemical and transport properties of 2,5-dimercapto-1,3,4-thiadiazole / poly(ethylene oxide) grafted polyaniline electrodes suffer from a loss of electronic conductivity. Decreasing of conjugation length with increasing of substituted aniline ring are responsible for the poor electrochemical and transport properties of the electrode and highly grafted polyaniline electrode [13].

In this work, grafted polymer electrode (GPE) was fabricated from 15%, 45% and 50% grafting percent of polystyrene with acrylonitrile using gamma irradiation. Using these new working electrodes was successful in cyclic voltammetry. GPEs were characterized electrochemically in aqueous electrolyte which proved good results.

2. EXPERIMENTAL

2.1. Synthesis of grafted polymer (GP)

Polystyrene grafted with acrylonitrile using gamma-irradiation technique was successfully synthesized. The new grafted polymer indicated that the best grafting percentage ratio could be

revealed when the concentration of the catalyst ferrous ammonium sulphate (FAS) is about 2% and the monomer concentration is 90%, at 1.25 Mrad dose [14].

2.2. Instruments and electro-analytical methods

Electrochemical workstations of Bioanalytical System Inc. USA: Model BAS 50W with potentiostat driven by electro-analytical measuring software were connected to a PC computer to perform cyclic voltammetry (CV) and chronocoulometry (CC). An Ag/AgCl (3M NaCl) and platinum wire (1mm diameter) were used as a reference and counter electrodes, respectively. The working electrode used in this study was Grafted Polymer Electrode (see below). The voltammetric experiments were carried out with 0.1M KCl as supporting electrolyte. Solution was degassed with nitrogen gas for ten minutes prior to recording the voltammogram.

2.3. Reagents

All reagents were analytical reagents or electrochemical grade purity. All solutions were prepared using distilled water. Unless otherwise specified, the supporting electrolyte used was 0.1M KCl in aqueous media at room temperature.

2.4. Preparing the new grafted polymer electrode (GPE)

GPE has been fabricated from grafted polymer. The percentage of grafted polymer and diameter of electrode were (15%, 45%, 50%) and 3 mm, respectively. A (1mm) hole was made to allow 1cm length of platinum wire out from the other side of electrode. A copper wire was then joined with the platinum wire.

After that, all parts of fabricated electrode were covered with glassy tube and then fixed with epoxy resin.

3. RESULTS AND DISCUSSION

3.1. Potential window of different electrodes in different grafted percentage

The working potential window of grafted polymer electrode was found to be in the range of (-1.8 - +1.8V) when using 15% grafted percentage working electrode as show in Figure (1c). Although the working window with anodic and cathodic peaks in the same regions when using 50% and 45% percentage of grafting as in Figure (1a) and (1b) respectively, it seems that redox current peaks of both electrodes of 50% and 45% significant many high current peaks.

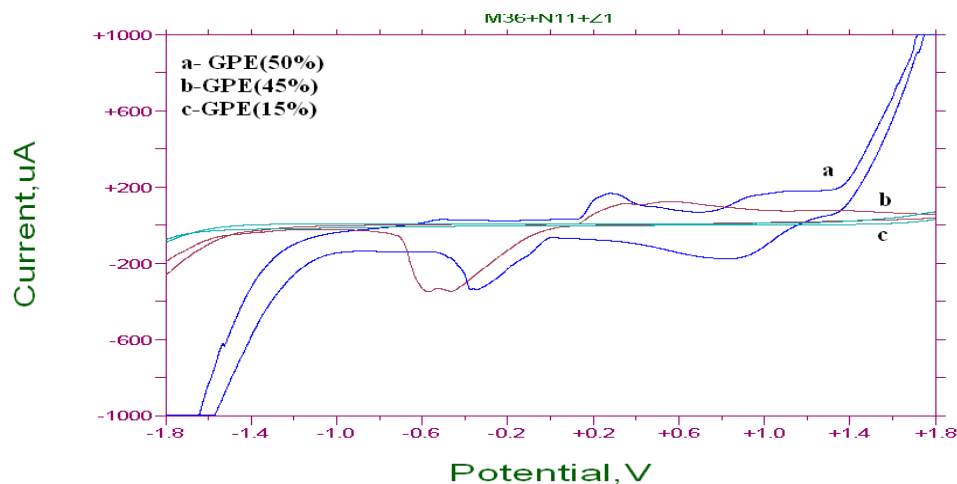


Figure 1. Cyclic voltammogram of different grafted polymer electrodes (a)GPE50% (b)GPE45% and (c)GPE15% in 0.1M KCl . SR=100mV/sec versus Ag/AgCl.

3.2. Affect the nature of anions in the electrolytes

The anion used in aqueous supporting electrolyte exerts highly influence on the redox current peaks of grafted polymer. Figure 2 shows that, in general redox current peaks of grafted polymer have dissimilar peaks formation, with the exception of KCl whose redox peaks, shown in (Figure 2.a), in the rang (-0.4 - +0.6V), while the redox peaks disappeared when using KNO_3 as shown in (Fig.2e).

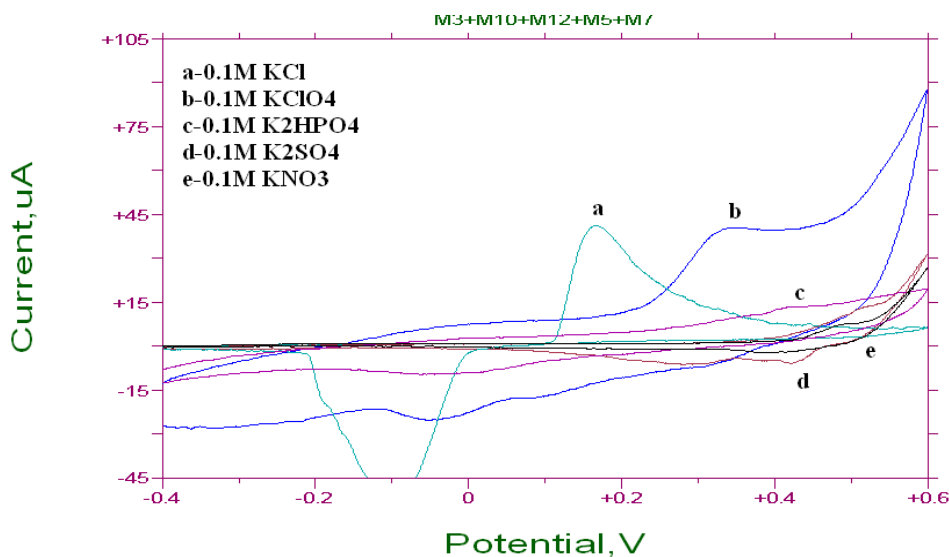


Figure 2. Cyclic voltammogram of GPE45% in different supporting electrolytes(in anion) at SR=100mV/sec versus Ag/AgCl.

3.3 Affect the nature of cations in the electrolytes

When different Groups of alkali-metal cations were used in the solution phase, the electrochemical redox of grafted polymer electrode (GPE 45% and 50%) showed a significant

variation. The most obvious change occurs in the redox potential, as shown in Table 1 and 2 (Figure 3.A, 3.B). It is clear that when the size of cation decreases, the grafted polymer electrode reduction potential shifts to more negative region and the oxidation potential peak shifts to more positive region. Thus, the size of cation increases and oxidation - reduction potential peaks of GPE (45% and 50%) become decreased in the following order: $\text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$. To explain this, one must take into consideration the electrochemical factors (such as conductivity and transport number) as well as the thermodynamic variation (such as enthalpy and free energy) which are affected by the sizes of cations. Based on thermodynamics, it is expected that any difference in radius of cation could have an influence on the hydration enthalpy, which will produce a change in Gibbs energy and electrical potential as summarized in Table 2 and 3 [15,16].

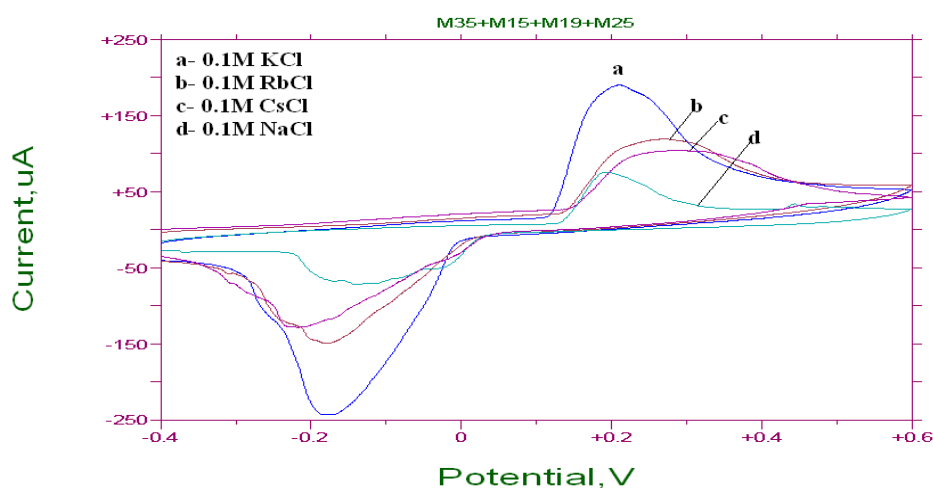


Figure 3a. Cyclic voltammogram of GPE 45% in different supporting electrolytes 0.1M of (KCl, RbCl, CsCl, NaCl), SR=100mV/sec versus Ag/AgCl.

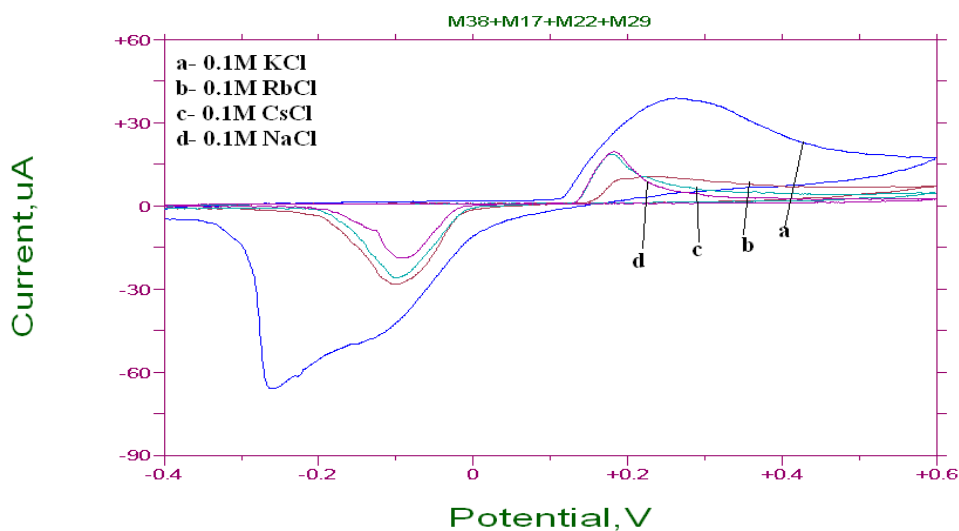


Figure 3b. Cyclic voltammogram of GPE 50% in different supporting electrolytes 0.1M of (KCl, RbCl, CsCl, NaCl), SR=100mV/sec versus Ag/AgCl.

Table 1. Redox peaks potential of GPE (45%) in 0.1M alkali-metal salts in water, scan rate of 100 mV/sec versus Ag/AgCl.

Cation	Epc mV	Epa mV
Na ⁺	-230.0	+285.9
K ⁺	-176.9	+210.0
Rb ⁺	- 181.5	+266.2
Cs ⁺	- 137.5	+188.8

Table 2. Redox peaks potential of GPE (50%) in 0.1M alkali-metal salts in water, scan rate of 100 mV/sec versus Ag/AgCl.

Cation	Epc mV	Epa mV
Na ⁺	-92.0	+182.7
K ⁺	-261.9	+263.1
Rb ⁺	-99.5	+232.8
Cs ⁺	-99.5	+179.7

Table 3. Comparison of crystal, hydrated ion radii, ionic conductivities, and hydration enthalpies for various first class alkali-metal cations [14, 15].

Cation	Crystal radii, r _i A ^o	Effective hydrated ion radii, r _s A ^o	Limiting ionic conductivities S cm ² equiv ⁻¹	Hydration enthalpies KJ mol ⁻¹
Cs ⁺	1.69	3.29	77.3	-263
Rb ⁺	1.48	3.29	77.8	-296
K ⁺	1.33	3.31	73.5	-321
Na ⁺	0.95	3.58	50.1	-405

3.4. Effect of varying amount of supporting electrolyte, KCl

Figure 4(A) and 4(B) show the cyclic voltammogram redox current peaks of grafted polymer electrodes (45% and 50%) respectively, in KCl of various concentrations ranging from 0.05 - 2.0 M. The redox current and potential of GPE 45% and GPE 50% were explained in Table 4 and 5, respectively. Table 6 shows the linear current dependent on KCl concentration observed at concentration range of (0.05 - 2M) which is described by a linear relationship. The slope of the linear

line for KCl showed that a considerably high sensitivity response of its current readily obtained at both GPE 45% and 50% electrodes during cyclic voltammetry.

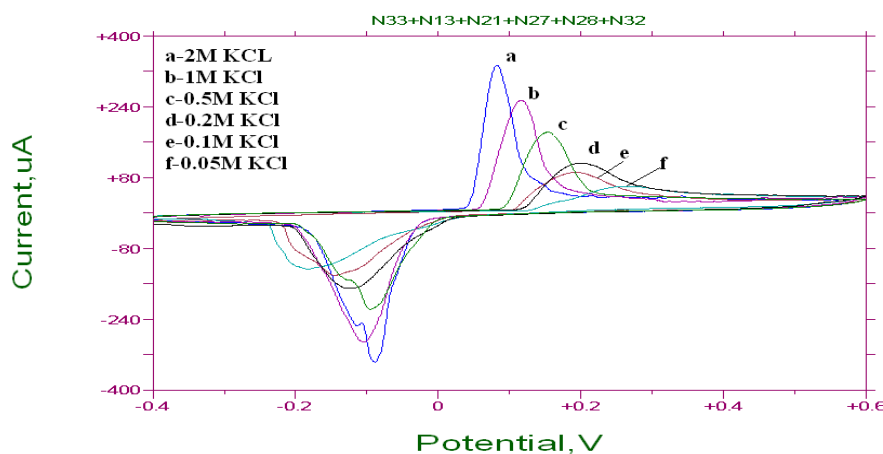


Figure 4a. Cyclic voltammogram of GPE45% in different concentrations of KCl (0.05, 0.1, 0.2, 0.5, 1 and 2M) SR=100mV/sec versus Ag/AgCl.

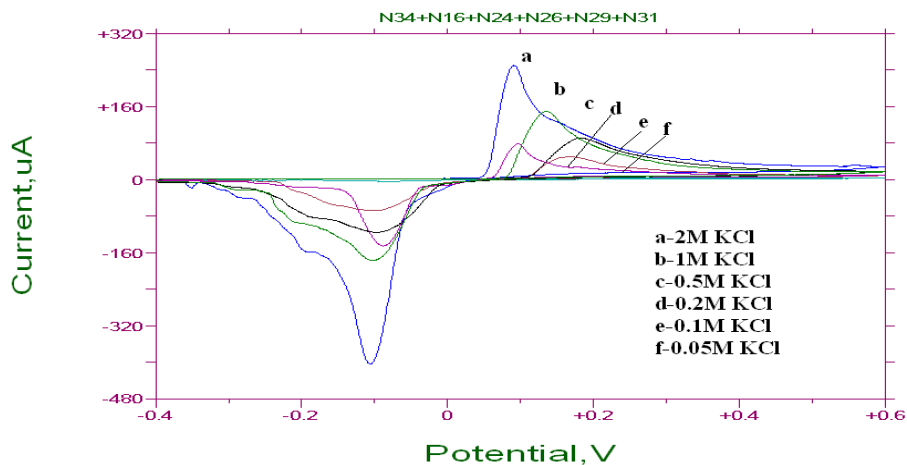


Figure 4b. Cyclic voltammogram of GPE50% in different concentrations of KCl (0.05, 0.1, 0.2, 0.5, 1 and 2M) SR=100mV/sec versus Ag/AgCl.

Table 4. Redox current peaks and potential of GPE (45%) in (2, 1, 0.5, 0.2, 0.1 and 0.05M) KCl, scan rate of 100 mV/sec versus Ag/AgCl.

Concentration, KCl (M)	Oxidation		Reduction	
	I _{pa} (uA)	E _{pa} (mV)	I _{pc} (uA)	E _{pc} (mV)
2	333.2	+82.5	337.2	-88.9
1	254.2	+117.5	292.7	-104.1
0.5	183.3	+153.9	215.7	-95.0
0.2	112.4	+197.9	169.1	-125.3

0.1	94.18	+193.3	140.8	-146.6
0.05	59.75	+272.2	126.6	-186.0

Table 5. Redox current peaks and potential of GPE (50%) in (2, 1, 0.5, 0.2, 0.1 and 0.05M) KCl, scan rate of 100 mV/sec versus Ag/AgCl.

Concentration, KCl (M)	Oxidation		Reduction	
	I _{pa} (uA)	E _{pa} (mV)	I _{pc} (uA)	E _{pc} (mV)
2	247.1	+90.1	403.0	-105.6
1	149.9	+135.7	178.2	-102.6
0.5	91.14	+182.7	145.8	-87.4
0.2	78.99	+96.2	117.5	-99.5
0.1	50.6	+164.5	66.84	-101.1
0.05	-	-	-	-

Table 6. Effect of different concentration of KCl (0.05, 0.1, 0.2, 0.5, 1 and 2M) on the redox current peaks of GPE45% and GPE50%:

GPE	Current(uA)	Slope(μ A/M)	Sensitivity
45%	cathodic	170.17	0.9899
45%	anodic	194.69	0.9674
50%	cathodic	163.63	0.9555
50%	anodic	99.939	0.9907

3.5. Effect of scan rate

Figure 5(A) and 5(B) show the cyclic voltammogram of grafted polymer electrodes 45% and 50%, respectively in 0.1M KCl at various scan rates. The result shows that the current of redox peaks increases with increasing scan rate. A reasonably linear dependence of GPE (50%) oxidative current on scan rate is described by $y=0.481X - 0.5905$, $R^2=0.9697$. The slope of graph Log I_{pa} (oxidative current) versus Log ν (scan rate) is 0.48; significantly differ from the theoretical value of half for diffusion- controlled process indicating the presence of a complex. Also, the relationship between oxidative potential and scan rate of GPE (50%), oxidation peak at 175mV in low scan rate has increased to 258.6mV in high scan rate. Linearly with equation $Y=0.0881X+175.05$ ($R^2=0.961$), the surface intercepts process at zero current produce zero current potential ($E^{0,1}$) of 175mV for the oxidation of GPE(50%).

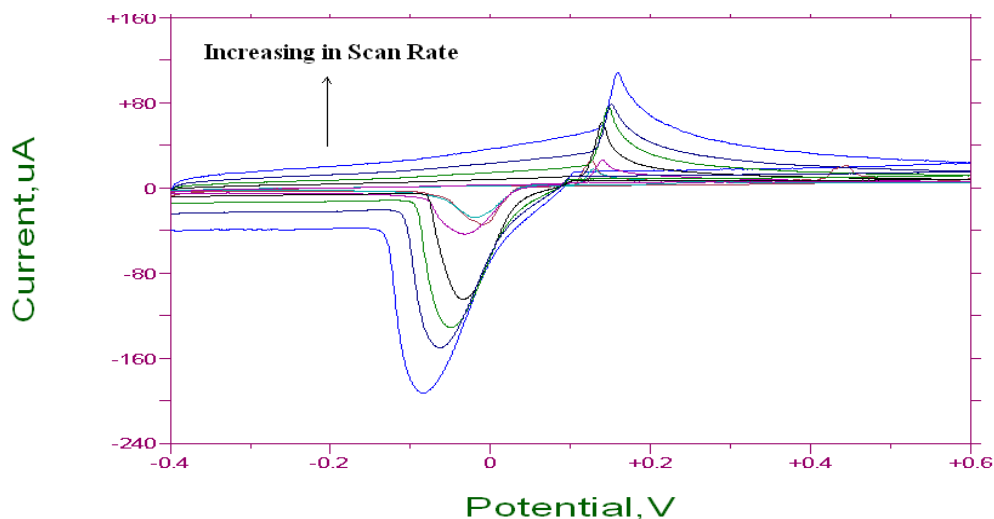


Figure 5a. Cyclic voltammogram of GPE %45 in different scan rate (5, 10, 50, 100, 250, 500, 1000mV/sec) in 0.1M KCl versus Ag/AgCl.

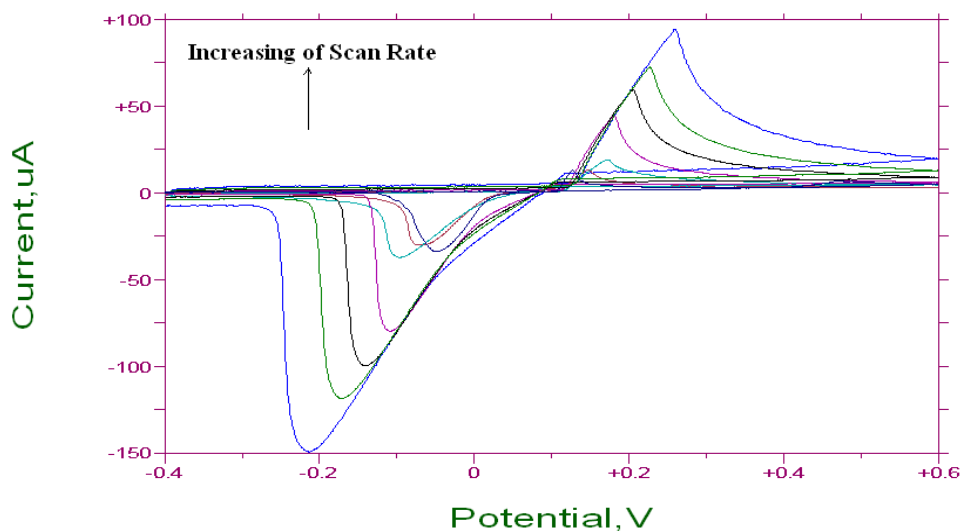


Figure 5b. Cyclic voltammogram of GPE %50 in different scan rate (5, 10, 50, 100, 250, 500, 1000 mV/sec) in 0.1M KCl versus Ag/AgCl.

3.6. Chronocoulometry of different grafted polymer electrodes

A double-step chronocoulometric experiment was carried out for different grafted polymer electrodes (GPE 15%, 45% and 50%) and in contact with 0.1M KCl aqueous electrolyte. It consists of an initial potential step from -400 to +600 mV and a reverse step from +600 to -400 mV. Figure 6 shows an Anson plot [17,18], it was found that the GPE in different grafted percentage (15%, 45% and 50%) have total charge transferred of 8.06, 7.00 and 4.97 $\mu\text{C}/\text{m}^2$, respectively. Thus, the grafted percentage of electrode increases and the total charge transferred on the surface of electrode decreases in the following order: GPE(15%) < GPE(45%) < GPE(50%). The electrochemical and charge

transferred of different grafted polymer electrodes have less of electronic conductivity versus increasing the percentage of FAS in the GPE [13].

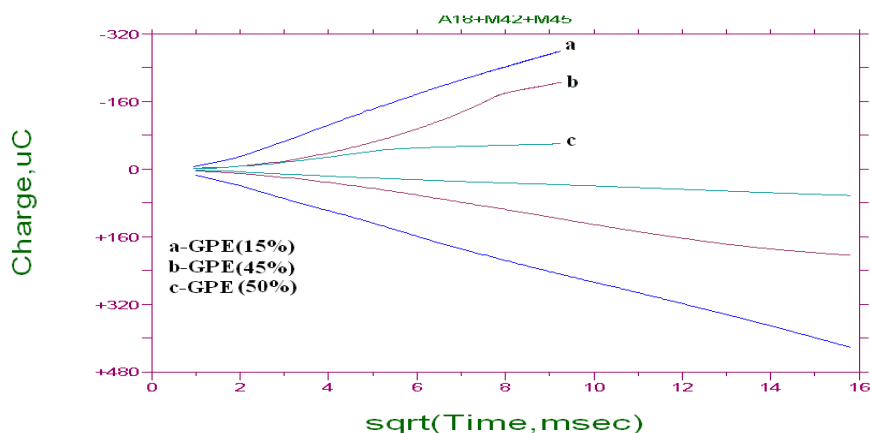


Figure 6. Chronocoulomogram or Anson plot of charge versus $t^{1/2}$ obtained for different grafted percentage of GPE (a) GPE15% (b) GPE45% and (c) GPE50% in 0.1M KCl as supporting electrolyte versus Ag/AgCl.

3.7. Effect of varying temperature

Effect of temperature on the oxidative peak of GPE (45%) was studied in 0.1M KCl. The current increases gradually temperatures between 10 to 90°C. Figure 7 is plot of log (oxidative current) of GPE (45%) versus reciprocal of temperature which is found to be fairly linear and is in agreement with thermodynamic expectation of Arrhenious equations 1 and 2 [19,20].

$$\sigma = \sigma^{\circ} \text{Exp} (- E_a/ RT) \text{-----} (1)$$

$$D = D^{\circ} \text{Exp} (-E_a/ RT) \text{-----} (2)$$

Where σ / D are conductivity / diffusibility and $\sigma^{\circ} / D^{\circ}$ are standard conductivity / the initial diffusibility. From the slope of linear relationship, the value of activated energy of GPE is $E_a = 6.32$ KJ/mol. The conductivity of GPE with increasing temperature also plays a significant influence on the activation energy for diffusion of the substrate of interest, E_a . Figure 8 shows that an increase in temperature from 10 to 85°C is accompanied by a sharp increase in current cases shifting of redox potential towards original. Evidently, simultaneous application of the use of GPE and increase in temperature were exist as a greater electrocatalyst effect in the electrochemical process of the new electrodes.

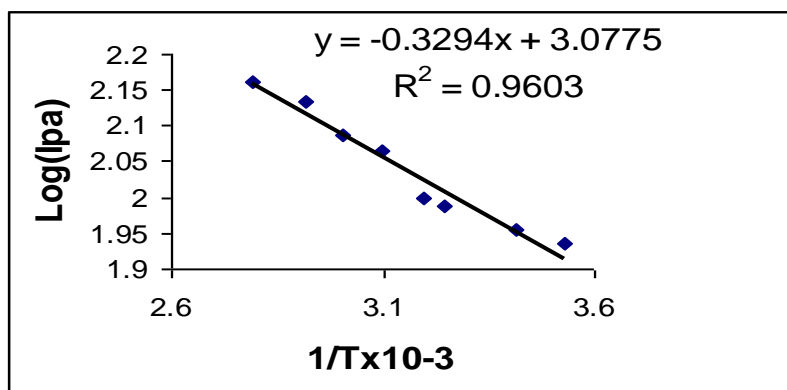


Figure 7. Dependence of oxidative current peak of GPE 45% as a function of temperature in 0.1M KCl at scanning rate 100 mV s^{-1} versus Ag/AgCl.

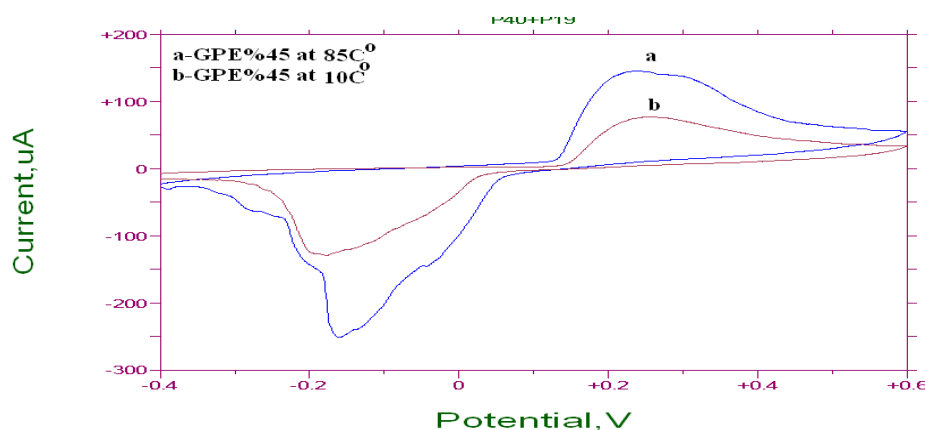


Figure 8. Cyclic voltammogram for the two redox peaks of GPE45% in 0.1M KCl Scan rate 100 mV s^{-1} versus Ag/AgCl as a reference electrode at (a) 10°C and (b) 85°C .

3.8. Effect of varying pH

The solution pH was varied from 2.0 to 12 in order to determine its effect on the catalytic redox peaks of GPE (45%) in 0.1M KCl as shown in Figure 9.

(a) Acidic pH solution was varied from 2 to 6 to determine its effect on the electrocatalytic redox peaks of GPE (45%). It was observed that the oxidation current of GPE 45(%) gradually and linearly increases with lowering of pH from 6 to 2 accompanied by a linear shift in oxidation potential which satisfies the linear equation of $I(\text{uA}) = -11.57 \text{ pH} + 178.71$ with correlation coefficient of $R^2 = 0.9489$ and $E(\text{mV}) = -8.2 \text{ pH} + 2412$ with correlation coefficient of $R^2 = 0.9761$. The reduction peak of GPE (45%) at -152.7 mV had shifted to a higher negative potential of -192.1 mV , with two fold increase of current.

(b) Alkaline pH solution from 10 – 12.5. It seems that the oxidation peak of GPE (45%) was affected by increasing alkaline which was solution shifted to lower potential at $+255.5 - 220.6 \text{ mV}$ with doubling the current value. There is a different property in basic media for the reduction peak which shifted to higher potential at $+183 - 228.5 \text{ mV}$ when increasing the current two times.

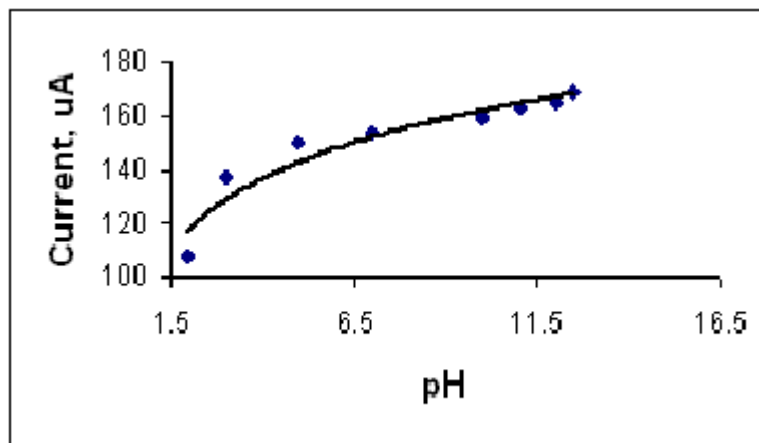


Figure 9. Reduction current for GPE(45%) in 0.1M KCl as a function of different pH(2-12.5) versus Ag/AgCl at a scan rate 100mV/sec.

3.9. Reproducibility

The potential cycling of the redox of GPEs in 0.1M KCl was carried out during cyclic voltammetry. Continuous potential cycling did not seem to affect the redox current of GPEs since the faradic activity appears reproducible even after 15 cycles reflecting the stability and reproducibility at the surface of GPE.

4. CONCLUSION

A redox potential scanning of different grafting percentage of Grafted Polymer Electrodes GPE (15%, 45%, 50%) immersed in aqueous solution containing potassium ions causes an irreversible electrochemical redox of GPE (45% and 50%) at the potential range of (-400 - +600) versus Ag/AgCl. In general, the redox current peaks of GPE is dependent on pH, temperature, scan rate, different cations and anions electrolyte and different concentration of KCl as supporting electrolyte. Excellent reproducibility of the current is observed, provided a freshly fabricated electrode is used for each experiment. Furthermore, the method for the fabrication of GPE is simple and cheap.

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References

1. G. Natta, P. Corradini and I. Bassi, *Nuovo Cimento*. 15 (1960) 68
2. T. Ong, S. Ng and H. Chan. *Synthesis, Polymer*. 44 (2003) 5597

3. A. Berlin, G. Zotti, S. Zecchin, G. Schiavon, M. Cocchi, D. Virgili and C. Sabatini, *J. Mat. Chem.* 13 (2003) 27
4. C. Chuy, J. Ding, E. Swanson, S. Holdcroft, J. Horsfall and K. Lovellb, *J. Electrochem. Soc.* 150 (2003) 271
5. T. Lee, Y. Shim and S. Shin, *Synthetic Metals.* 126 (2002) 105
6. H. Peng, L. Zhang, C. Soeller and J. Sejdic, *Biomaterials.* 30 (2009) 2132
7. B. Adhikari and S.Majumdar, *Prog. Polym. Sci.* 29 (2004) 699
8. C. Fanga, C. Yia, Y. Wanga, Y. Caoa and X. Liua, *Biosensors and Bioelectronics.* 24 (2009) 3164
9. M. Radhi, *Sensors and Transducers J.* 125 (2011) 168
10. M. Radhi, M. Jobyer and A.Mehde, *Sensors and Transducers J.* 137 (2012) 66
11. H. Hossein, M. Dabiri and M. Ashrafi, *Poly. Intern.* 55 (2006) 1081
12. S. Hosseini, J. Simia and B. Farhadpour, *Iran. Poly. J.* 18 (2009) 3
13. H. Moon and J. Park, *Solid State Ionics.* 120 (1999) 1
14. W. Tan, M. Radhi, M. Rahman and A. Kassim, *J. Appl. Sci.* 10 (2010) 139
15. J. Burgess, *Ions in solutions: basic principles of chemical interactions.* Ellis Horwood, Chichester, (1988).
16. B. Conway, *Ionic hydration in chemistry and biophysics.* Elsevier, Amisterdam, (1981).
17. Instruction manual, CV 50W, version 2. Bioanalytical System, Inc. USA, Feb, (1996).
18. A. Bard and L. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd Ed. Wiley, New York, (2001).
19. W. Tan and J. Goh, *J. Electroanalysis.* 20: 2008: 2447-2453.
20. S. Jacob, Q. Hong, B. Coles, R. Compton, *J. Phys. Chem.* 103 (1999) 2963