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Electrochemical Properties of Polyacrylic Acid Film on Gold, Platinum and Glassy Carbon Electrodes in Aqueous Solutions

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Abstract:
In this paper, we demonstrate for the first time that modifying glassy carbon (GC), gold (Au) and platinum (Pt) working electrodes with poly acrylic acid (PAA) enhances their rate of electron transfer at the electrode-polymer interface. Cyclic voltammeter of potassium ferricyanide on all the electrodes (Au, Au/PAA, Pt, Pt/PAA, GC and GC/PAA) used in this work gave a one reduction and one oxidation peak supporting the well known single redox step for Fe(III)/[Fe(II). The formal redox potentials ($E^{o'}$) for this system were found to be 0.142V for Au, 0.058V for Au/PAA, 0.057V for Pt, 0.017V for Pt/PAA, 0.222V for GC and 0.063V for GC/PAA versus Ag/AgCl. While the apparent heterogeneous rate constant (k_s) for the Au/PAA and GC/PAA modified electrodes were 100 times higher compared to plain Au and plain GC electrodes. For Platinum electrodes, k_s values for Pt/PAA were 15 times higher compared to those of plain Pt. The diffusion coefficient (D_o) found were as follows: $0.003x10^{-7}cm^2/s$ (Au), Au/PAA was $1.790x10^{-7}cm^2/s$(Au/PAA), $0.004x10^{-7}cm^2/s$(Pt), $0.016x10^{-7}cm^2/s$(Pt/PAA), $0.001x10^{-7}cm^2/s$(GC) and $0.032x10^{-7}cm^2/s$(GC/PAA). Overly, this indicates that the PAA modified electrodes carries enormous potential in electro analysis.

Keywords: *Polyacrylic acid, glassy carbon, gold and platinum electrodes, cyclic voltammeters, electrochemical properties.*

1. Introduction

There is a growing interest in modifying electrodes by derivatizing, polymer-coating, functionalizing and/or electrostatic-binding specific molecules to the surface. This process of modifying electrode surfaces deliberately and controllably produce electrodes with new and interesting properties that has formed the basis of various applications of electrochemistry. In most cases the layer or coating made on the electrode surface is electroactive, that is, it can exchange electrons with the underlying substrate material and be oxidized or reduced, although some applications of nonelectroactive films have also been used [1 - 7].

Polyacrylic acid (PAA) is a three-dimensional cross-linked polymer network that swells by absorbing water up to hundreds of times its own weight, hence called a superabsorbent [8]. PAA has a variety of applications including drug delivery devices [9], biomaterial for tissue engineering [10], in agriculture [11], and waste water treatment [12], based on its ability to absorb water and to adsorb and retain dissolved substances, such as dyes [13] and heavy metal ions that have environmental impact [14].

We had used this polyacrylic acid/glassy carbon electrode (PAA/GCE) system before to develop electrochemical sensors to analyze Pb, Cd and Co heavy metals in drinking waters simultaneously [15, 16]. But background information concerning the electrochemical, particularly the electrokinetic properties of these PAA modified working electrodes is lacking. Therefore, this work reports the electrokinetic properties of the PAA modified electrodes in aqueous solutions using potassium ferricyanide as the electrochemical probe. Various electrode materials including gold, platinum and glassy carbon were considered. Results reported in this work demonstrate that modifying a glassy carbon, gold and platinum electrodes with PAA improve their rate of electron transfer at the electrode-solution interface. The key electrochemical technique used in this study is cyclic voltammeter (CV) because of its relative simplicity and its high-performance content [17].

2. Experimental

2.1. Chemicals and Solutions

All the chemicals used were of analytical grade quality and were used without further purification. The chemicals used included; poly (acrylic acid), 25wt% solution in water, potassium ferricyanide (AR), acetic acid glacial (AR) and sodium acetate anhydrous (AR) were from fisher scientific and were used as received. For voltammetry, the electrolyte was acetate buffer. Water was purified to specific resistivity >15 MΩ cm. All other chemicals were reagent grade.

2.2. Apparatus

All the electrochemical experiments were performed with a CHI 1232B electrochemical workstation (CH Instruments, Inc., USA). A three-electrode system (CH Instrument Inc., USA) consisted of a modified glassy carbon working electrode with diameter of 3 mm, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode. A pH meter Bench – Model CyberScan pH Tutor (Eutech Instruments) was used for all pH measurement. All experiments were carried out in a 10.0mL electrochemical cell at room temperature. All data were analyzed using Kaleidagraph software, version 4.1.1.

2.3. Cleaning of the Glassware

All the glass wares used in this work were thoroughly cleaned by soaking them in nitric acid and sulphuric acid mixtures for 48 hours, followed by cleaning with detergent, ordinary water and finally rinsing them with de-ionized water.

2.4. Polyacrylic acid Film Preparation and Optimization

Glassy carbon disk electrodes (3 mm diameter) were abraded on wet silicon carbide paper (400 grit, Buehler) followed by (600 grit, Buehler) [21]. Rinsed in water, then polished thoroughly with 0.05 micron micropolish (CH Instruments) slurry on a soft cloth before sonicated in ethanol and distilled water for 3 min each to remove particles and other possible contaminants [22]. The actual surface area was 0.071cm^2. 10µL of freshly prepared 4mM polyacrylic acid were deposited on the polished electrode and allowed to react at room temperature for 20 minutes. Then the electrodes were rinsed with de-ionized water before use.

2.5. Electrochemical Characterization of the PAA/GCE

Standard potassium ferricyanide solution was used to characterize the plain GC, Pt and Au and PAA/GC, PAA/Pt and PAA/Au electrodes. Diffusion coefficients for the standard potassium ferricyanide redox couples were determined by cyclic voltammetry at the electrodes using Randles-Sevcik equation. Then Nicholson method was used to calculate the apparent heterogeneous rate constant (k). Anodic and cathodic peak separations from a background subtracted voltammogram were used to evaluate ψ from which k was obtained using equation 1:

$$\psi = \frac{k}{(aD_o)^{1/2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where D_o is the diffusion coefficient and a = nFv/RT (v being the scan rate).

3. Results and Discussions

Cyclic voltammetry of potassium ferricyanide on all the electrodes (Au, Au/PAA, Pt, Pt/PAA, GC and GC/PAA) used in this work gave a one reduction peak and one oxidation peak (*figures 1a, 2a and 3*). It is interesting to note that the reduction and oxidation potentials for the plain electrodes compares relatively well with those of polyacrylic acid modified electrodes. The slight difference particularly with respect to the shape of the voltammogram can be attributed to the slight change in the surface chemistry of the modified electrodes.

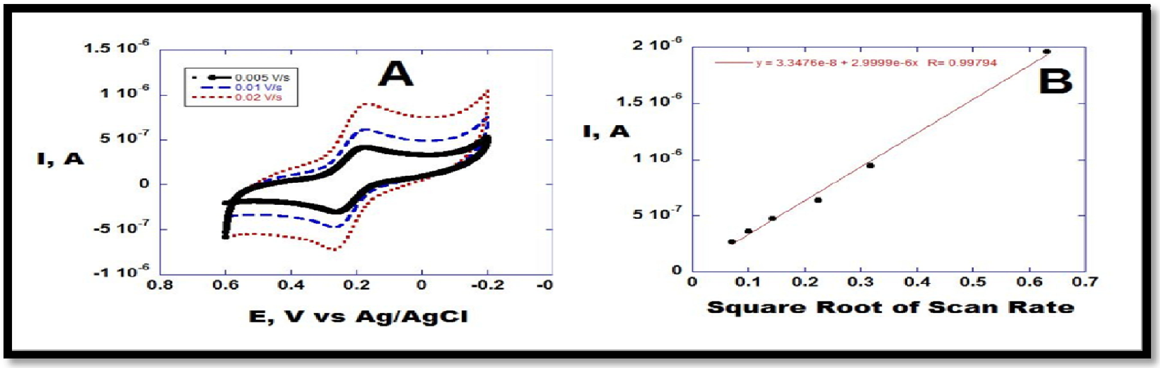

Figure 1: (A) Cyclic Voltammeter of 1.0mm Potassium Ferricyanide at Scan Rate Of 0.005 V/S To 0.02 V/S. The Electrolyte Was 0.1M Potassium Chloride
(B) Plot of Current (A) Versus Square Root of Scan Rates on Plain Glassy Carbon Electrode

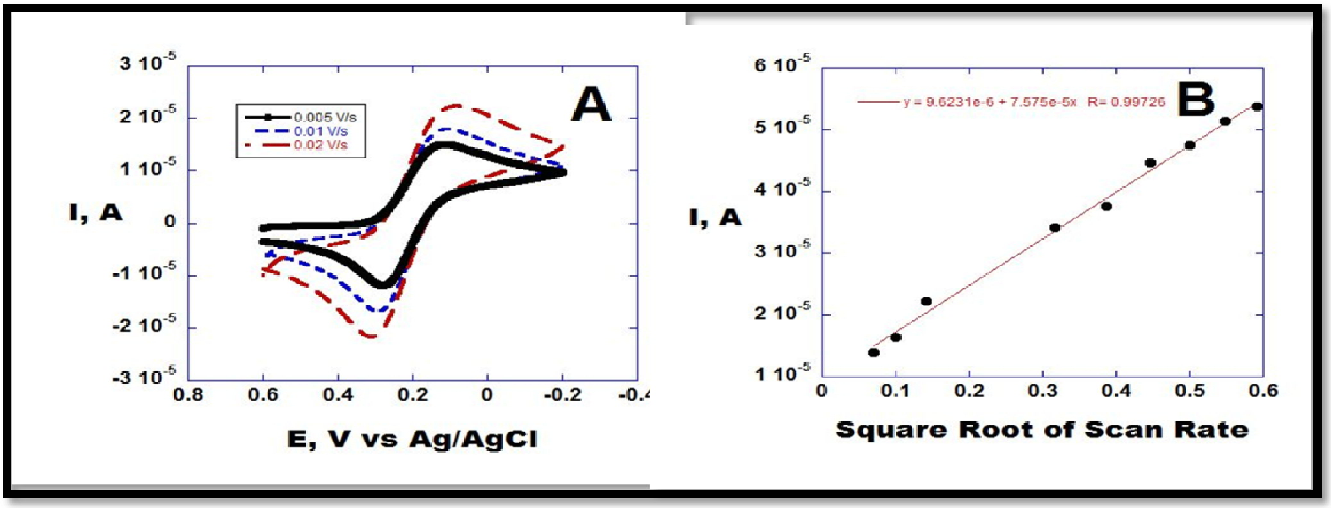

*Figure 2: **(A)** Cyclic Voltammeter of 1.0mm Potassium Ferricyanide at Scan Rate of 0.005 V/S to 0.02 V/S. The Electrolyte Was 0.1M Potassium Chloride*
***(B)** Plot of Current (A) Versus Square Root of Scan Rates on Polyacrylic Acid/Glassy Carbon Electrode (PAA/GCE)*

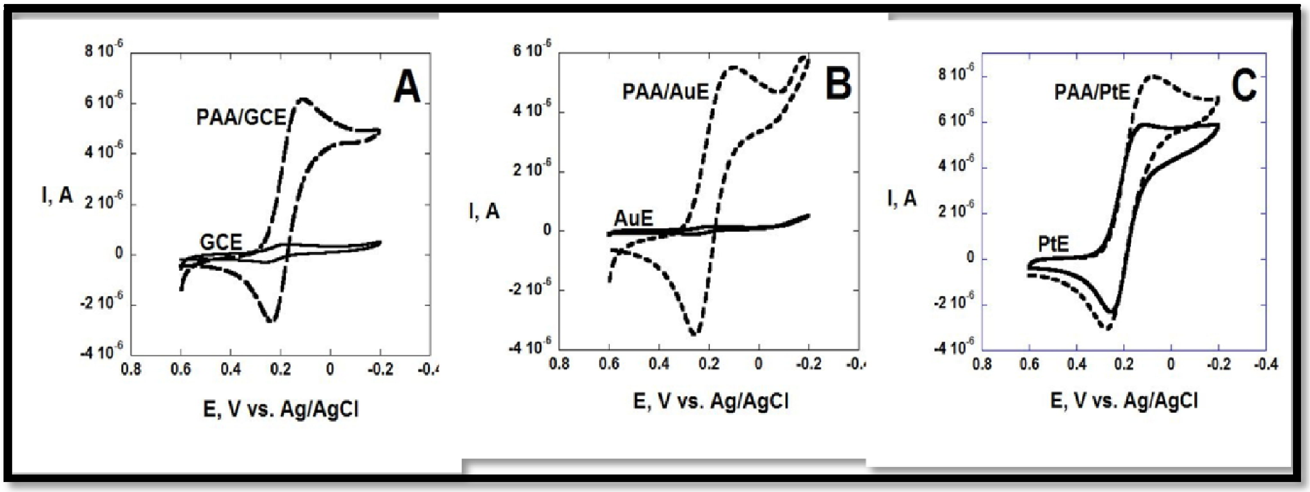

Figure 3: Cyclic Voltammograms of 1.0mm Potassium Ferricyanide at Scan Rate Of 0.005 V/S On (A) GCE and PAA/GCE (B) Aue and PAA/Aue (C) Pt and PAA/Pt. The Electrolyte Was 0.1M Potassium Chloride

The reduction and oxidation voltammetric currents for the potassium ferricyanide in 0.1M potassium chloride solutions increased with increase in scan rate on all the electrodes (figure 1a and 2a). The anodic to cathodic peak ratio (I_a/I_c) were almost unity in both media. The number of electrons (n) involved in the redox responses for potassium ferricyanide was obtained from the slope of the plots of potential, E, versus log[i/i_d-i], equation 2 [17].

$$E = E_{1/2} - \frac{0.0591}{n}\log\left(\frac{i}{i_d - i}\right) \text{..} (2)$$

Where E is the potential at any point on the wave, $E_{1/2}$ is the half-wave potential, i_d is the peak current, i is the current at any point on the wave and n is the number of electrons exchanged in the radix process. Accordingly, n was found to have a value of 1 for the potassium ferricyanide in 0.1M potassium chloride solutions on Au, Au/PAA, Pt, Pt/PAA, GC and GC/PAA electrodes. This in turn supports the single radix step for Fe (III)/ [Fe (II) radix mentioned earlier.

Formal radix potential ($E^{o'}$) for a reversible system is taken to be the mid-point between the reduction (E_c) and oxidation (E_a) potentials. As shown from table 1, the $E^{o'}$ obtained were 0.142V for Au, 0.058V for Au/PAA, 0.057V for Pt, 0.017V for Pt/PAA, 0.222V for GC and 0.063V for GC/PAA versus Ag/AgCl. This data shows that the mid-point potential for the PAA modified electrodes are more negative while those of plain electrodes were more positive. Thus, the Fe (III)/Fe (II) redox process is accomplished with less energy for the PAA modified electrodes compared to plain electrodes.

No.	ELECTRODE	$E^{o,}$ (V)	D_c, $x10^{-7}$ (cm^2/s)	k^o_c, $x10^{-3}$(cm/s)
1	Au	0.142	0.003	0.028
2	Au/PAA	0.058	1.790	3.870
3	Pt	0.057	0.004	0.235
4	Pt /PAA	0.017	0.016	1.640
5	GC	0.222	0.001	0.088
6	GC/PAA	0.063	0.032	9.074

Table 1: Electrochemical Properties for the Gold, Platinum and Glassy Carbon Electrodes
$D_{c\,=}$ Diffusion Coefficient (Catholic); $E^{o,}$ = Formal Radix Potential; K^o_c = Apparent Heterogeneous Rate Constant (Cathodic)

Methods developed by Laviron [18] and Hirst and Armstrong [19] were applied to compute the rate of electron transfer between the electrode and the analyte. By compensating for the constant peak separations (ΔE_p) at low scan rates, plots of the resulting data for the electron transfer between electrode and the diffusing analyte species were made. Assuming the electron transfer coefficient to be $\alpha = 0.5$, the apparent electrochemical electron transfer rate constants were estimated [20]. The k_s results obtained (table 1) show that the k_s values for the Au/PAA and GC/PAA modified electrodes were much higher by almost 100 times compared to plain Au and plain GC electrodes. For Platinum electrodes, k_s values for Pt/PAA were higher by about 15 times compared to those of plain Pt. Overly, PAA modified electrodes had higher apparent electrochemical electron transfer rate constants compared to unmodified electrodes.

Following Randles-Sevcik equation 3 [17], plots of reduction currents (i_{pc}) versus the square root of scan rates ($\nu^{1/2}$) between 0.005 V/s and 0.1 V/s were made (*figures 1b and 2b*). Linear plots were obtained whose slopes were used to obtain the diffusion coefficients (*table 1*) on all the electrodes.

$$i_{pc} = (2.69\times 10^5) n^{3/2} C^{*} A D^{1/2} \nu^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where i_{pc} is the diffusion peak current, n is the number of electrons exchanged in the redox process, C^* is the concentration of potassium ferricyanide, A is the area of the electrode, D is the diffusion coefficient and ν is the scan rate. The linear plots obtained (*figure 1b and 2b*) indicate that the electrode processes are all diffusion controlled. From table 1, the D_o for Au was $0.003x10^{-7}cm^2/s$ while Au/PAA was $1.790x10^{-7}cm^2/s$. For Pt was $0.004x10^{-7}cm^2/s$ while for Pt/PAA was $0.016x10^{-7}cm^2/s$. Those for GC plain was $0.001x10^{-7}cm^2/s$ while GC/PAA was $0.032x10^{-7}cm^2/s$. Overly, PAA modified electrodes had higher diffusion coefficients compared to unmodified electrodes. Of the six electrodes, GC/PAA had the highest diffusion coefficient, followed by Au/PAA then Pt/PAA.

All these data indicate that modifying Au, Pt and GC electrodes with polyacrylic acid enhances the diffusion coefficients and the rate of electron transfer at the electrode-polymer interface. These and similar electrodes carries enormous potential in electroanalysis.

4. Conclusion

Modifying glassy carbon, gold and platinum working electrodes with polyacrylic acid (PAA) enhances rates of electron transfer at the electrode/polymer interface. These PAA modification process produces new electrodes with enormous potential in electroanalysis.

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