CHAPTER 10

Poly(diallyldimethylammoniumchloride)-(polystyrenesulphonate-Hexacyanoferrate (II) composite) modified graphite electrode by layer by layer technique for the oxidation of Ascorbic acid

- Construction of Gr/(PDDA/PSS-[Hexacyanoferrate(II)]₄) electrode
- Characterization
- Applications in ascorbic acid detection
Abstract

Through layer-by-layer adsorption (LBL) technique, the positively charged poly (diallyldimethylammoniumchloride) and negatively polystyrenesulphonate- Hexacyanoferrate (II) composite multilayer film was formed on Graphite electrode. The resulting modified electrode was chemically stable and was used to electrocatalytically oxidize ascorbic acid in phosphate buffer solution. The modified electrode was characterized by cyclic voltammetry and electrochemical impedance spectroscopy. Chronoamperometric studies showed the linear relationship between oxidation peak current and the concentration of ascorbic acid in the range 25-350 μM (R=0.998) with the detection limit of 0.1 μM (S/N=3). Further, dopamine and uric acid do not interfere in the detection of ascorbic acid.
10.1. Introduction

Modified electrodes have been widely used as sensitive and selective sensors in various electro analytical methods. Among the various mediators available for modification, hexacyanoferrate (II) was used as suitable modifier due to excellent electron transfer properties [1]. Most of the modified electrodes have been used to reduce the over potential and also to overcome the slow kinetics of many electrode processes.

Ascorbate (vitamin C) is water soluble substance present in a wide number of fruits and vegetables. Due to the presence of ascorbate in the mammalian brain, it has an important role in bioelectrochemistry, neurochemistry and clinical diagnostics applications. This is necessary for the formation of collagen, and has been used for the prevention and treatment of common cold, mental illness, scurvy and cancer. The content of ascorbate in biological fluids can be used to assess the amount of oxidation stress in human metabolism, and extensive oxidative stress has been linked to cancer, diabetes mellitus and hepatic disease. Therefore, the determination of ascorbate contents is particularly important in the pharmaceutical and food industry at different concentration levels [2, 3].
10.2. The construction of the of (PDDA/PSS-[Hexacyanoferrate(II)]₄) electrode modified graphite electrode is discussed in the chapter three, Section 3.5

10.3. Characterization

10.3.1. Cyclic voltammetry

The electrochemical behavior of bare graphite and modified electrodes in 0.1 M phosphate buffer solution is as shown in Figure 10.1(A). Well defined peaks at 0.221 and 0.131 V were observed with $\Delta$Ep of 0.09 V for the bare electrode. After modifying the electrode with (PDDA/PSS-[Hexacyanoferrate (II)]₄), a well defined redox peaks at 0.074 and -0.043 V was observed with $\Delta$Ep of 0.117 V for the modified electrode at a scan rate of 0.5 V s⁻¹. The shift in peak potential may be due to positively charged layer of PDDA which attracts the negatively charged PSS-[Hexacyanoferrate (II)]₄. The cathodic and anodic peak currents increased linearly with increase in the number of bilayers, suggesting uniform growth of each bilayer as shown in Figure 10.1(B). The linear equations were

\[
i_{pa} = 5.85 \times 10^{-4} + 2.17 \times 10^{-4} N_L \quad (R = 0.998) \quad \textbf{10.1}
\]

\[
i_{pc} = -8.08 \times 10^{-4} - 1.74 \times 10^{-4} N_L \quad (R = 0.987) \quad \textbf{10.2}
\]

Where $N_L$ is the number of bilayers.

The modified electrode remained unaltered on continuous potential cycling and repetitive measurements, suggesting that the positively charged PDDA and the negatively charged PSS-[Hexacyanoferrate(II)]₄ layers are bound strongly to each other through electrostatic interaction.
10.3.2. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy is an effective method for probing the features of surface-modified electrodes using the redox probe Fe(CN)$_6^{4-}$-$3^-$. Figure 10.2 shows that at bare graphite electrode the impedance spectrum was composed of a semicircle and a straight tail line. The semicircle part at high frequency corresponds to limited electron-transfer process and the linear part at low frequency originates from the mass transfer limitation of Fe(CN)$_6^{4-}$-$3^-$. Interestingly after modifying the graphite electrode with PDDA and PSS-[Hexacyanoferrate (II)]$_4$, the semicircle was not observed and only a straight line was observed suggesting diffusion controlled electron transfer process. Because PDDA and PSS are excellent electric conducting materials, they could accelerate the electron transfer and resulted in the reduction of charge transfer resistance [4]. This indicates that the impedance offered by modified electrode-electrolyte interface for charge transfer process is less compared to the bare electrode. Impedance decreases as the number of bilayers increases (figure not shown) [4]. The decrease in resistance observed in the impedance plots is a good evidence for the increase in current observed in CV profiles.

Figure 10.1: Cyclic voltammograms (A) of (a) bare graphite electrode, (b) bare Gr in 3mM Fe(CN)$_6^{4-}$-$3^-$ and (c) Gr/(PDDA/PSS-[Hexacyanoferrate(II)]$_4$) modified electrode. (B) Cyclic voltammograms of Gr/(PDDA/PSS-[Hexacyanoferrate(II)]$_4$) modified electrode, where n=1-5 (a-e) in phosphate buffer solution of pH 7.0 at a scan rate of 0.05 V s$^{-1}$.
10.4. Electro catalytic oxidation of AA at Gr/(PDDA/PSS-[Hexacyanoferrat(II)₄]) electrode

Figure 10.3 shows the ascorbic acid oxidation on Gr/(PDDA/PSS-[Hexacyanoferrat(II)₄]) electrode surface. The cyclic voltammetry curve in the presence of 6 mM ascorbic acid at pH 7.0 shows a considerable enhancement of the electrode anodic peak current at 0.19 V (curve b) in comparison with the peak current in the absence of ascorbic acid (curve a). The acid oxidation reaction at the solid-solution interface can be described by the following reaction

\[
2(\text{Gr/PDDA-PSS-}[\text{Fe(CN)}₆^{4-}\]) \rightarrow 2(\text{Gr/PDDA-PSS-}[\text{Fe(CN)}₆^{3-}\]) + 2e \quad \text{....................... 10.3}
\]

\[
2(\text{Gr/PDDA-PSS-}[\text{Fe(CN)}₆^{3-}\]) + \text{H}_₂\text{AA} \rightarrow 2(\text{Gr/PDDA-PSS-}[\text{Fe(CN)}₆^{4-}\]) + 2\text{AA} + 2\text{H}^+ \quad \text{.... 10.4}
\]

Where H₂AA is the ascorbic acid and AA the dehydroascorbic acid.
10.4.1. Effect of increasing concentration at Gr/(PDDA/PSS-[Hexacyanoferrate(II)]₄) electrode

The cyclic voltammogram responses for a series of AA solution with various concentrations are shown in Figure 10.4. With the addition of AA there was an increase in the anodic peak current linearly. The linear regression equation is given by

\[ i_{p(\text{AA})}(\text{A}) = 0.0015 + 1.24\times10^{-4}C_{\text{AA}}(\text{mM}), \quad R = 0.997, \quad SD = 1.7\times10^{-5} \]  

Figure 10.4: Cyclic voltammograms of Gr/(PDDA/PSS-[Hexacyanoferrate(II)]₄) for varying AA concentrations of 0, 1, 2, 3, 4, 5 and 6 mM (a-g) in phosphate buffer solution at pH 7.0 containing 0.1 M KCl at a scan rate of 0.05 V s⁻¹. Inset: The calibration curve;
10.4.2. Effect of scan rate at Gr/(PDDA/PSS-[Hexacyanoferrat(II)]₄) electrode

Figure 10.5 shows the cyclic voltammograms recorded for 6 mM AA solution in different scan rates. It is observed that by increasing the sweep rate, the peak potential for the oxidation of AA shifts to more positive values. The peak currents for the anodic oxidation of AA are proportional to the square root of scan rate, predicting a diffusion controlled process [6]. The inset in the figure shows the relation between scan rate and anodic peak current and the linear regression equation is given by

\[ i_p(A) = -7.6 \times 10^{-5} + 2.6 \times 10^{-4} v \ (V \ s^{-1}), \quad R = 0.997, \quad SD = 7.2 \times 10^{-5} \]

Figure 10.5: Cyclic voltammograms of Gr/(PDDA/PSS-[Hexacyanoferrate(II)]₄) at different scan rates (a-k) 0.05, 0.075, 0.1, 0.125, 0.15, 0.175, 0.2, 0.0225, 0.25, 0.275 and 0.3 V \ s^{-1} in a solution containing 6 mM AA. Inset: Plot of \( i_p \) vs (scan rate)\(^{1/2} \)

10.4.3. Constant amperometric determination of AA at Gr/(PDDA/PSS-[Hexacyanoferrate(II)]₄) electrode

Figure 10.6 shows the amperogram recorded for the Gr/(PDDA/PSS-[Hexacyanoferrate(II)]₄) electrode at a working potential of +0.1 V with successive additions of AA into the 0.1 M phosphate buffer solution at pH 7.0. The reaction occurring at the Gr/(PDDA/PSS-[Hexacyanoferrate(II)]₄) electrode was very fast, reaching a
dynamic equilibrium upon each addition of the analyte with a response time less than 3 s to reach 100% signal. Such a fast amperometric response time is indicative of faster charge transport on the modified electrode. A wide linear response range from 25-350 μM was observed and the linear regression equation is

\[ I_{\text{pNADH}} (A) = 7.7 \times 10^{-5} + 5.2 \times 10^{-7} C_{\text{AA}} (\mu M), \quad R = 0.998, \quad SD = 3.0 \times 10^{-6} \]

A sensitivity of 1.9 μA cm\(^{-2}\) μM\(^{-1}\) was obtained. The detection and quantification limits were estimated at 0.1 μM (S/N=3) and 5 μM respectively.

Figure 10.6: Chronoamperometric response of Gr/(PDDA/PSS-[Hexacyanoferrat(II)]\(_n\) electrode for the oxidation of AA at +0.1 V in phosphate buffer solution (pH 7.0). Each addition increased the concentration of AA by 25 μM. Inset: plot of [AA] vs. catalytic peak current.

10.4.4. Interference studies

We investigated the effect of interfering species commonly found in biological samples such as DA and UA as shown in Figure 10.7. The addition of AA to the stirred solution shows the increasing current response, however, the addition of interfering species such as DA (50 μM) and UA (50 μM) did not show any current response. The prepared modified electrode is good for AA sensor.
10.5. Stability and reproducibility

Long term stability is one of the most important requirements of biosensors. The stability of Gr/(PDDA/PSS-[Hexacyanoferrate(II)]$_4$) electrode was checked in the presence of 1 mM AA by performing amperometric experiment in 0.1 M phosphate buffer solution of pH 7.0 at an applied potential of +0.1 V under stirring condition for a period of 30 min. Figure 10.8 shows that the decrease of current observed was less than 2% even in stirring condition indicating that the modified electrode is stable and suitable for sensor application. The modified electrode showed an acceptable repeatability. The interface was prepared eight times in the same manner and tests performed in 0.1 M phosphate buffer at pH 7.0 a relative standard deviation lower than 5% was obtained indicating good repeatability of the preparation of the sensor.
10.6. Conclusion

In this work, the electrocatalytic oxidation of AA at Gr/(PDDA/PSS-[Hexacyanoferrate(II)]) electrode has been investigated. The electrochemical oxidation of AA is a diffusion controlled process. The modified electrode also offers stable amperometric detection of AA at an applied potential of +0.1 V with a linear range of 25-350 μM and detection limit of 0.1 μM. The modified electrode showed diminished response from its interferences and the surface fouling was not observed during voltammetric and amperometric measurement of AA.
10.7. References


