

Ferrocenium Ion Encapsulated Montmorillonite Clay Modified Glassy Carbon Electrode For The Detection Of Ammonium Sulphide In The 10^{-7} Molar Range

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Abstract: In this paper it is found that ferrocene shows well-defined reversible cyclic voltammograms ($P^H=7.0$, Tris buffer; Ag-AgCl, 0.1M $NaNO_3$) for the Fc^+ @Clay/Styrene/GC electrode in phosphate buffer (p^H 7.0) containing 0.1 M $NaNO_3$. This paper embodies ferrocene encapsulated Montmorillonite Clay modified GC electrodes for the determination of trace amount of ammonium sulphide in solution. The redox currents of the modified electrode decreases to different extent on it's interaction with ammonium sulphide.

Index terms: Ferrocene, Montmorillonite clay, cyclic voltammetry, ammonium sulphide, voltammetric sensor

I INTRODUCTION

Detection and determination of small bio molecules and metal ions are of great importance for diagnosis of a number of diseases and understanding environmental pollution leading to extensive research on development of chemical sensors. Chemical sensors have a chemical or molecular target to be measured. More useful definition for a chemical sensor is - a small device that as a result of a chemical interaction or process between the analyte and the device, transforms chemical or biochemical information of a quantitative or qualitative type into an analytically useful signal¹. A number of spectroscopic and chromatographic methods like UV/Visible, Fluorescence, High Performance Liquid Chromatography (HPLC), Atomic Absorption Spectroscopy (AAS), Mass Spectroscopy (MS) etc are known for analysis of small bio molecules and metal ions. The prime disadvantages of these methods are – High cost, Special condition to run (HPLC, AAS, MS) and often requiring to derivatise the analyte involving complicated organic reactions. Among different sensors, electrochemical sensors are unique because of simplicity, low cost, easy maintenance, high dynamic range, easy to handle and easy in vivo applications². Voltammetric sensor, one of the major constituents of electrochemical sensors, is essentially a surface modified working electrode (WE). The modifying agents may be surfactants, lipids, zeolites, clays etc. to name a few with or without a probe molecule^{3,4}.

Montmorillonite is a very soft phyllosilicate group of minerals that is typically formed in microscopic crystals, forming clay. Montmorillonite, a member of the smectite family, is 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately one micrometre. Members of this group include saponite. It is the main constituent of the volcanic ash weathering product, bentonite. It may have played a central role in the evolution of life. The water content of montmorillonite is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. Clay modified

electrode as electrochemical sensor is an area of rapid growth.

II DETAILS EXPERIMENTAL

This paper embodies ferrocene encapsulated Montmorillonite clay modified GC electrodes for the determination of trace amount of ammonium sulphide in solution. The redox currents of the modified electrode decreases to different extent on it's interaction with ammonium sulphide.

II.1 Encapsulation of ferrocenium ion into Montmorillonite clay:

0.42g of Ferrocene was taken in 75 ml of distilled water. Concentrated HNO_3 was added dropwise till the solution becomes blue in color. To the solution 1.0 g of Montmorillonite clay was added and followed by stirring for 48 hours. The suspension was then filtered and washed many times with distilled water and dried in desiccator. The ferrocenium encapsulated Montmorillonite clay will hereafter be designated as Fc^+ @Clay.

II.2 Preparation of Fc^+ @Clay film on GC electrode:

1.0 g of Fc^+ @Clay and 0.1 mL of styrene was taken in 5 mL of Tetrahydrofuran (THF) and stirred for 30 minutes. 20 μ L of the suspension was placed on the tip of a GC electrode and allowed to evaporate at room temperature to obtain a film of Fc^+ @Clay. This modified electrode will be designated as Fc^+ @Clay/Styrene/GC in the further discussions.

III RESULTS AND DISCUSSIONS

III.1 Electrochemical characterization of Fc^+ @Clay/Styrene/GC electrode:

Fig1. shows the cyclic voltammogram for the Fc^+ @Clay/Styrene/GC electrode in phosphate buffer (p^H 7.0) containing 0.1 M $NaNO_3$.

Fig2. shows the cyclic voltammogram for the Fc^+ @Clay/Styrene/GC electrode at different scan rates in phosphate buffer (p^H 7.0) containing 0.1 M $NaNO_3$. The

redox potential value $E_{1/2}$ is 0.4995 V and peak separation $\Delta E_p = 0.131$ V at scan rate 0.1 Vs^{-1} . The result confirms that ferrocenium ion has been encapsulated into the clay.

The Charge versus time response in double potential step Chrono Coulometry experiment of $\text{Fc}^+@ \text{clay}/\text{Styrene}/\text{GC}$ electrode in phosphate buffer ($\text{p}^{\text{H}} 7.0$) containing 0.1 M NaNO_3 shows electrochemical response due to ferrocene/ferrocenium couple confirming encapsulation of ferrocene in montmorillonite (Fig 3). Fig.4 shows square wave voltammogram of $\text{Fc}^+@ \text{Clay}/\text{Styrene}/\text{GC}$ electrode in phosphate buffer ($\text{p}^{\text{H}} 7.0$) containing 0.1 M NaNO_3 , reference electrode Ag-AgCl (3 M NaCl)

III.3 Effect of ammonium sulphide on redox properties of modified electrode:

Fig.5 shows the cyclic voltammogram of $\text{Fc}^+@ \text{Clay}/\text{Styrene}/\text{GC}$ electrode when ammonium sulphide is added into the electrolytic medium. The oxidation and reduction currents decreased with ammonium sulphide concentration. The plot of the reduction current versus the concentration of ammonium sulphide is shown in Fig 5. The current decreases from $4.5 \mu\text{A}$ to $1.0 \mu\text{A}$.

IV. CONCLUSION:

In this report it is found that ferrocene shows well-defined reversible cyclic voltammograms ($\text{P}^{\text{H}}=7.0$, Tris buffer; Ag-AgCl, 0.1M NaNO_3) for the $\text{Fc}^+@ \text{Clay}/\text{Styrene}/\text{GC}$ electrode in phosphate buffer ($\text{p}^{\text{H}} 7.0$) containing 0.1 M NaNO_3 . The redox potential value $E_{1/2}$ is 0.4775 V and peak separation $\Delta E_p=0.083$ V at scan rate 0.1 Vs^{-1} . The result confirms that ferrocenium ion has been encapsulated into Clay. In this report, it has been observed that both the cathodic and anodic peak currents decrease when ammonium sulphide is added to the electrolytic solution and become zero when the thiourea concentration is (15-30) μM . The peak becomes undetectable when concentration of ammonium sulphide is $15 \mu\text{M}$. The plot of cathodic and anodic current versus concentration of ammonium sulphide is linear

FIGURES:

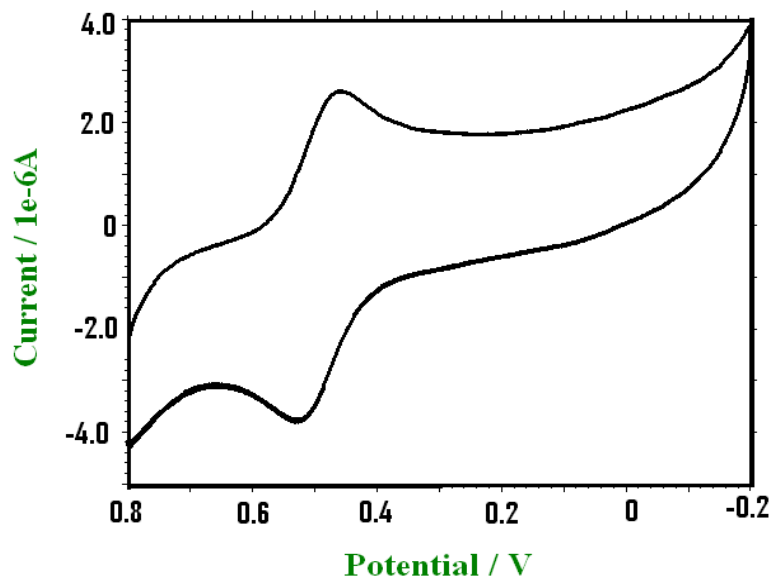


Fig1: Cyclic voltammogram of $\text{Fc}^+\text{@Clay/Styrene/GC}$ electrode in phosphate buffer (pH^{H} 7.0) containing 0.1 M NaNO_3 , reference electrode Ag-AgCl (3 M NaCl).

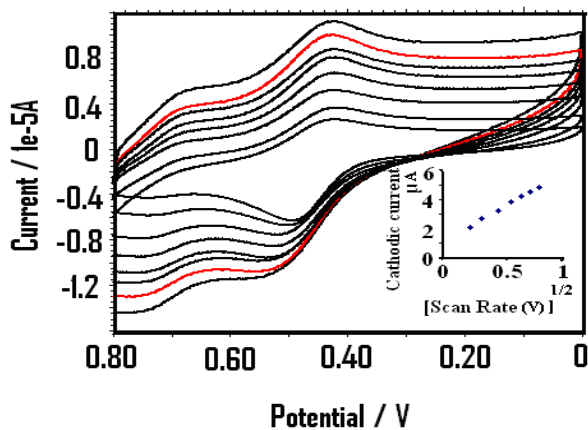


Fig 2: Cyclic voltammogram of $\text{Fc}^+\text{@Clay/Styrene/GC}$ electrode at various scan rates in phosphate buffer (pH^{H} 7.0) containing 0.1 M NaNO_3 , reference electrode Ag-AgCl (3 M NaCl). (Inset: The plot of cathodic currents versus square root of scan rate is found to be linear)

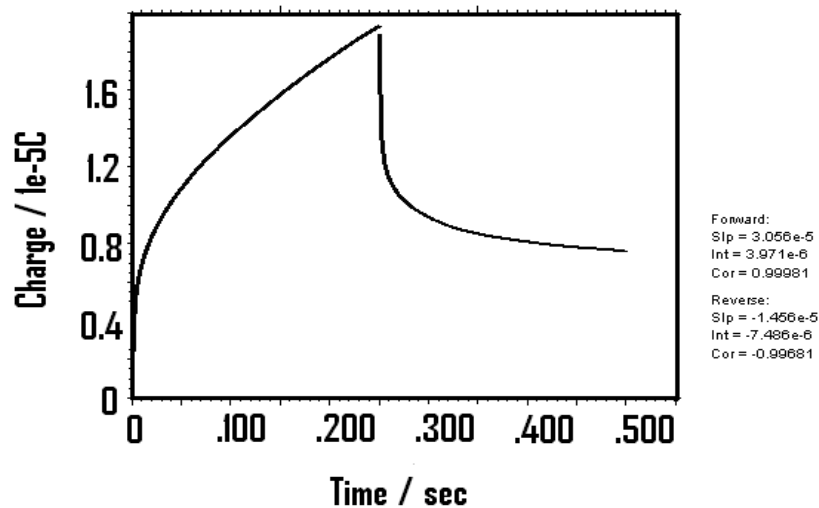


Fig 3: Charge versus time response in double potential step Chrono Coulometry experiment of Fc^+ @Clay/Styrene/GC electrode in phosphate buffer (p^{H} 7.0) containing 0.1 M NaNO_3 , reference electrode Ag-AgCl (3 M NaCl).

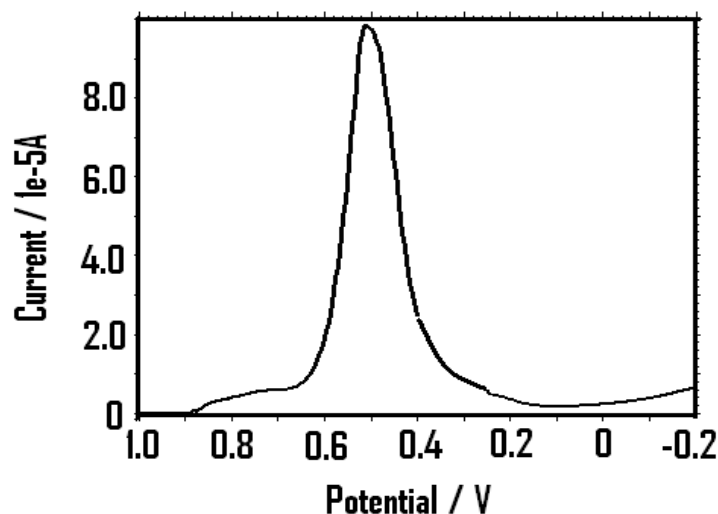


Fig4: Osteryoung square wave voltammogram of Fc^+ @Clay/Styrene/GC electrode in phosphate buffer (p^{H} 7.0) containing 0.1 M NaNO_3 , reference electrode Ag-AgCl (3 M NaCl)

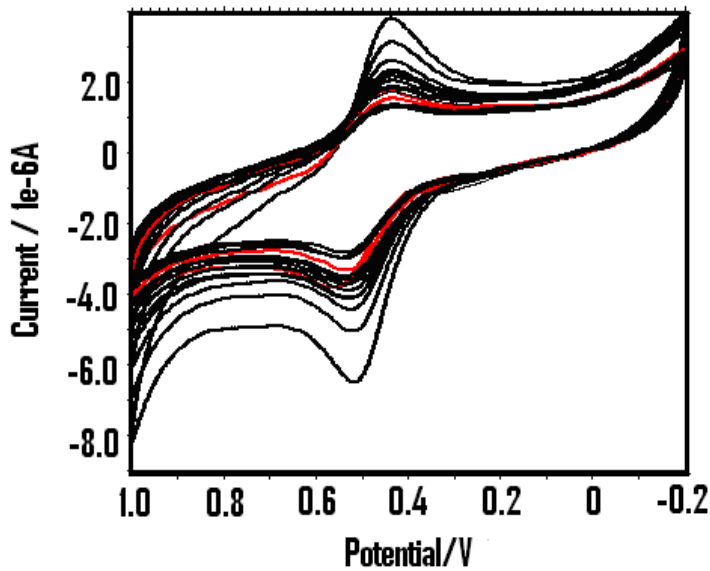


Fig 5: Cyclic voltammetric response of Fc^+ @Clay/Styrene/GC electrode when ammonium sulphide is added into the electrolytic medium. The currents due to oxidation and reduction process decreases.

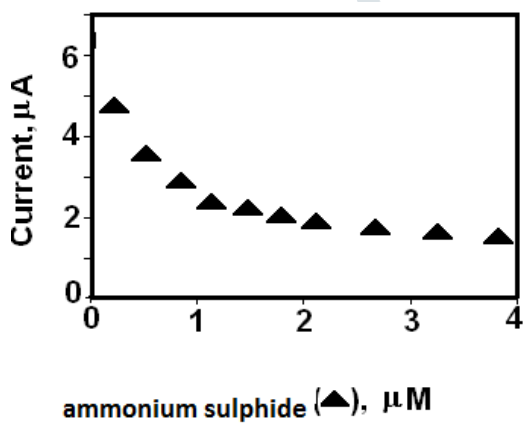


Fig 5 Cyclic voltammetric response of Fc^+ @Clay/Styrene/GC electrode when ammonium sulphide is added into the electrolytic medium. The currents due to oxidation and reduction process decreases.

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