

Amperometric determination of hydrazine at manganese hexacyanoferrate modified graphite–wax composite electrode

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Abstract

Fabrication, characterization and application of a manganese hexacyanoferrate (MnHCF) modified graphite–wax composite electrode are described. The MnHCF mixed with graphite powder was dispersed into molten paraffin wax to yield a conductive composite, which was used as electrode material to construct a renewable three-dimensional MnHCF modified electrode. The characterization of the modified electrode has been studied by electrochemical techniques. The cyclic voltammogram of the MnHCF modified graphite–wax composite electrode prepared under optimum composition, showed a well-defined redox couple due to $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ system. The electrocatalytic oxidation of hydrazine by MnHCF modified graphite–wax composite electrode has been investigated in an attempt to develop a new sensor for its determination. It was found that the mediator catalyzed the oxidation of hydrazine. The electrocatalytic oxidation of hydrazine was also studied under hydrodynamic and chronoamperometric conditions. The anodic current increases linearly with increase in the concentration of hydrazine in the range of 3.33×10^{-5} M to 8.18×10^{-3} M. The detection limit was found to be 6.65×10^{-6} M ($S/N=3$). The modified electrode can also be used for on-line detection of hydrazine. The proposed method has also been applied for the determination of hydrazine in photographic developer solution.

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1. Introduction

The development of novel electrode materials for use in the determination of clinically, industrially and environmentally important compounds is currently an area of very active investigation. Hydrazine (N_2H_4) and its derivatives have been found to have wide applications in industry, agriculture, as explosives, antioxidants, photographic developer, oxygen scavengers and propellants. Hydrazine is a base product in fuel cell [1] and also is very important in pharmacology because it has been recognized as a carcinogenic and hepatotoxic substance, which affects liver and brain [2]. The detection and determination of N_2H_4 becomes essential in view of its importance in diverse context and thus there is a growing need for the development of simple, economical and accurate on-line monitoring devices for determination of trace amounts of hydrazine in different samples such as water, industrial and environmental materials.

Several techniques such as spectrophotometry [3], coulometry [4], amperometry [5], potentiometry [6], titrimetry [7] and chemiluminescence [8] have been reported for the determination of hydrazine. The direct oxidation of hydrazine has been studied at several electrodes including mercury [9,10], silver and gold [10], platinum [11] and nickel [12]. Although metals such as Pt, Au, and Ag are very active in the anodic oxidation of hydrazine, they are too expensive for practical applications and require a large overpotential for hydrazine determination.

A major attention has been focused on the development of chemically modified electrodes during the last two decades. They exploit the ability of certain surface-bound redox mediators to enhance electron-transfer kinetics and thus lower the operating potential. Hence relatively large amounts of electrochemical research have been devoted to the development and application of different types of chemically modified electrodes. Wang et al. [13] described a modified electrode based on 3,4-dihydroxy benzaldehyde for the remote monitoring of hydrazine. A few transition metal complexes are efficient electrocatalyst for the anodic oxidation of hydrazine [14–16]. One important group of inorganic compounds utilized for electrode modification and

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electrocatalytic purpose is the transition metal hexacyanoferrates. Scharf and Grabner [17] used a Prussian blue (PB) modified glassy carbon electrode for the electrocatalytic oxidation of hydrazine. Electrocatalytic efficiency of various transition metal hexacyanoferrate modified graphite electrodes for the oxidation of hydrazine has been reported [1]. The objective of the present study is to fabricate and characterize a new amperometric sensor utilizing MnHCF modified graphite–wax composite electrode for hydrazine determination. The composite electrode was prepared using graphite powder, MnHCF and paraffin wax, which act as conductor, mediator and binder, respectively.

2. Experimental

2.1. Instrumentation

A Fourier-transform infrared (FT-IR) spectrum for the MnHCF complex was obtained using Perkin-Elmer Spectrum (I Model) and elemental analysis of MnHCF complex was conducted with a Perkin-Elmer Optima Emission Spectrometer (ICP-OES). Electrochemical investigations were carried out with the EG&G PAR Electrochemical System (Model 263A) equipped with GPIP (IEEE-488) interface port and IBM personal computer. A MnHCF modified graphite–wax composite electrode and a platinum wire were used as working and counter electrode, respectively. The reference electrode was a saturated calomel electrode (SCE). All experiments were carried out at room temperature (25 °C) under nitrogen atmosphere.

2.2. Materials and reagents

Graphite powder (1–2 μm , synthetic) was obtained from Aldrich. Hydrazinium chloride was purchased from Sigma. Manganese sulphate and potassium ferrocyanide were from Merck. Other chemicals employed were of analytical grade and used without further purification. All solutions were prepared using bidistilled water. pH variation was carried out by adjusting the pH of the electrolyte solution using HCl and NaOH and 0.05 M phosphate buffer was used when the pH was maintained at 7. The commercial samples analyzed were photographic developer solution obtained from a local photographic studio.

2.3. Preparation of MnHCF complex

The MnHCF complex was prepared by precipitation via the drop-wise addition of 0.1 M MnSO_4 to a well-stirred solution of 0.1 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ in a beaker [1]. After the addition, the mixture was stirred well for 15 min and kept undisturbed for an hour, the precipitate was then centrifuged with repeated washing using 0.1 M NaCl, followed by distilled water. The dried precipitate was then ground to a fine powder. We also confirmed that the composition of the complex is $\text{Na}_2\text{Mn}[\text{Fe}(\text{CN})_6]$ by elemental analysis and from the typical infrared absorption at 2066 and 485/594 cm^{-1} for CN and FeCN/FeC, respectively. These results indicate that the complex obtained is MnHCF species, which is in agreement with previous studies [18].

2.4. Fabrication of MnHCF modified graphite–wax composite electrode

The MnHCF modified graphite–wax composite electrode was prepared by thoroughly mixing 0.650 g of graphite powder and 0.050 g MnHCF particles in an agate mortar for at least 10 min. The above mixture was then added to 0.300 g of melted paraffin wax. The liquid paste was mixed thoroughly, transferred into a glass tube with 4 mm inner diameter and 4 cm length, and then packed tightly in the tube. After solidification and removal from the tube, the electrode was obtained in the form of a rod and it was coated with molten paraffin. The paraffin was removed at both ends, at the top for making electrical connection and at the bottom to provide the sensor surface. The modified electrode consists 5% (w/w) of mediator and it produced the best current response. Hence, MnHCF modified graphite–wax composite electrode with 5% mediator was used for all experiments. Similarly an electrode with same composition of graphite powder and paraffin wax without the mediator was also prepared and used as the bare electrode.

3. Results and discussion

3.1. Electrochemical behavior of MnHCF modified electrode

The electrochemical behavior of the bare and MnHCF modified graphite–wax composite electrode as working electrodes was studied by recording cyclic voltammograms in 0.1 M NaCl in the potential range of -0.4 to 0.8 V at a scan rate of 20 mV/s. The results obtained are shown in Fig. 1. The curve a represent the electrochemical response of the bare electrode, which was found to be insignificant. The curve c corresponds to the voltammogram for MnHCF modified graphite–wax electrode, which shows a pair of redox peaks with anodic peak at 0.44 V

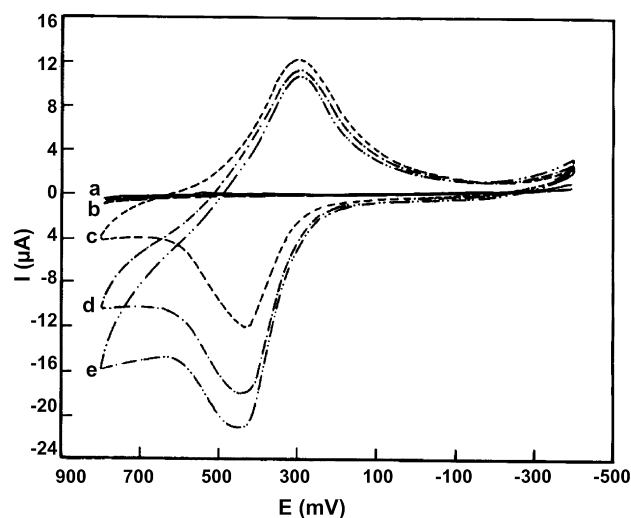


Fig. 1. Cyclic voltammogram in 0.1 M NaCl for (a) bare electrode, (b) 1.27×10^{-4} M N_2H_4 at bare electrode, (c) MnHCF modified, graphite–wax composite electrode, (d) 1.27×10^{-4} M and (e) 1.87×10^{-4} M N_2H_4 at MnHCF graphite–wax modified electrode. Scan rate: 20 mV/s.

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