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# Preparation of poly N,N-dimethylaniline/ferrocyanide film modified carbon paste electrode: Application to electrocatalytic oxidation of L-cysteine

Reza Ojani *, Jahan-Bakhsh Raoof, Ebrahim Zarei

*Electroanalytical Chemistry Research Laboratory, Faculty of Chemistry, Mazandaran University, Babolsar, Iran*

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ABSTRACT

Functionalized poly N,N-dimethylaniline film was prepared by adsorption of ferrocyanide onto the polymer forming at the surface of carbon paste electrode (CPE) in aqueous solution. The electrocatalytic ability of poly N,N-dimethylaniline/ferrocyanide film modified carbon paste electrode (PDMA/FMCPE) was demonstrated by oxidation of L-cysteine. Cyclic voltammetry and chronoamperometry techniques were used to investigate this ability. In the optimum pH (6.00), the electrocatalytic ability about 480 mV and the catalytic reaction rate constant, ($k_h$), can be seen $3.08 \times 10^3\ M^{-1}\ s^{-1}$. The catalytic oxidation peak current determined by cyclic voltammetry method was linearly dependent on the L-cysteine concentration and the linearity range obtained was $8.00 \times 10^{-5}$ –$2.25 \times 10^{-3}$ M. Detection limit of this method was determined as $6.17 \times 10^{-5}$ M ($2\sigma$). At a fixed potential under hydrodynamic conditions (stirred solution), the calibration plot was linear over the L-cysteine concentration range $7.40 \times 10^{-6}$ M–$1.38 \times 10^{-4}$ M. The detection limit of the method was $6.38 \times 10^{-6}$ M ($2\sigma$).

## 1. Introduction

Polymer modified electrodes (PMEs) prepared by electropolymerization have received interest in the detection of analytes because of its selectivity, sensitivity and homogeneity in the electrochemical deposition, strong adherence to electrode surface and chemical stability of the film [1,2]. Selectivity of PMEs as a sensor can be attained by different mechanisms such as size exclusion [3], ion exchange [4] and hydrophobic interaction [5]. In this context, some electroactive conducting polymers themselves exhibit catalytic effects for any redox reactions, e.g. reduction of nitrite on poly(ortho-toluidine) [6] and oxidation of hydrazine on polyaniline [7], but in order to increase this catalytic activity, several strategies have been developed by incorporating chemical species into the polymer matrix, which can mediate the electron transfer process. These mediators can be metal particles [8], enzymes [9] and doping ions [10]. Among the doping ions ferrocyanide was used as an ion incorporated into polymer films in order to, e.g. electrocatalysis of ascorbic acid oxidation [11] and simultaneously determination of dopamine and ascorbic acid [12].

Electropolymerization of N,N-dialkylaniline (DAA) for example dimethyl on electrode surface has been studied by many group [13–15]. The anion exchange property and electrode kinetics of metal incorporated into the polymer films were studied [13,14]. Also by using poly N,N-dimethylaniline (PDMA) the simultaneous detection of dopamine in the presence of ascorbic acid was carried out [16].

On the other hand, cysteine is of great importance in biological and biomedical processes. Being an important amino acid in protein structures, cysteine participates in a number of biochemical processes which depend directly on the particular reactivity of thiols. Its oxidized derivatives have additional metabolic functions. Many methods for its determination have been reported including spectrophotometry [17–19], fluorimetry [20–22], electrophoresis [23], high performance liquid chromatography [24] and electrochemical methods [25–27]. Of these, voltammetric techniques offer high sensitivity and selectivity for cysteine determination. However, at most conventional electrodes, the oxidation of cysteine occurs at high positive potentials. Therefore, several chemically modified electrodes (CMEs) have been designed for the electrocatalytic oxidation of cysteine [28–30]. Recently, we have prepared some modified carbon paste electrodes and used for electrocatalytic oxidation and determination of some biologically important compounds [31–33].

In the present paper, we prepared poly N,N-dimethylaniline (PDMA) film by the anodic oxidation of N,N-dimethylaniline (DMA) at the surface of carbon paste electrode (CPE). The PDMA is shown to be an ionene polymer with positively sites as quaternized ammonium groups in the polymeric backbone (Scheme 1). Therefore, the positively charged sites of this polymer film strongly attract the multiply charged anions, e.g. $Fe(CN)_6^{4-}$ by anion exchange with the supporting electrolytic anions, e.g. $SO_4^{2-}$ initially

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* Corresponding author. Tel.: +98 112 5242025 7; fax: +98 112 5242029/5242002.

*E-mail address:* fer-o@umz.ac.ir (R. Ojani).

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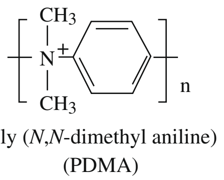

**Scheme 1.** Structure of poly N,N-dimethylaniline (PDMA).

present in the film for forming poly N,N-dimethylaniline/ferrocyanide film modified carbon paste electrode (PDMA/FCNMCPE). To the best of our knowledge, no study with PDMA/FCNMCPE for voltammetric determination of L-cysteine has been reported. Thus, in this study we present and discuss the electrochemical properties and electrocatalytic determination of L-cysteine at the surface of poly N,N-dimethylaniline/ferrocyanide film modified carbon paste electrode. The catalytic reaction rate constant, ($k_h$), between L-cysteine and electrogenerated ferricyanide into bulk polymer was determined by chronoamperometry.

## 2. Experimental

### 2.1. Reagents and materials

The solvent for electrochemical studies was doubly distilled water. The N,N-dimethylaniline and L-cysteine from Fluka and $K_4Fe(CN)_6$ from Merck were used as received. High viscosity paraffin (density: 0.88 g $cm^{-3}$) from Fluka and graphite powder (particle diameter: 0.10 mm) from Merck was used for preparation of working electrode. Buffer solutions were prepared from $H_2SO_4$, NaOH, $H_3PO_4$ and its salts for pH range of 2.00–11.00.

### 2.2. Preparation of working electrode

A 1:1 (w/w) mixture of graphite powder and paraffin was blended by hand mixing with a mortar and pestle for preparation of carbon paste. The resulting paste was then inserted in the bottom of a glass tube (internal radius: 0.30 mm). The electrical connection was implemented by a copper wire lead fitted into the glass tube.

### 2.3. Instrumentation

Electrochemical experiments were carried out using a potentiostat/galvanostat (Bhp2061-C Electrochemical Analysis System, Behpajooh, Iran) coupled with a Pentium III personal computer connected to a HP Laser Jet 6 L printer. A platinum wire was used as the auxiliary electrode. A carbon paste electrode as working electrode and a double junction Ag|AgCl|KCl(3M) electrode as reference electrode were used. A pH-meter (Ion Analyzer 250, corning) was used to read pH of buffer solutions.

### 2.4. Preparation of PDMA/FCN film

The PDMA/FCN film modified carbon paste electrode was prepared in the following way. The carbon paste electrode (CPE) was immersed in aqueous solution containing 0.15 M N,N-dimethylaniline, 0.50 M $Na_2SO_4$ and $H_2SO_4$ (pH 1.00) buffer. The electropolymerization was performed potentiostatically by holding the potential of the working electrode at 1.00 V versus the reference electrode for 15 min. The obtained film was washed with $H_2SO_4$ solution (pH 1.00) and then distilled water. For incorporation of $Fe(CN)_6^{4-}$ into PDMA film, this electrode was immersed in 0.24 mM $Fe(CN)_6^{4-}$ and potential was scanned for three stages between −0.2 and 0.8 V. This modified electrode was washed with distilled water before being used.

## 3. Results and discussion

### 3.1. Electrochemical behavior of $Fe(CN)_6^{4-}$ incorporated into the PDMA

Studies show that poly N,N-dimethylaniline immobilized at surface of carbon paste electrode is noneletroactive (Fig. 1a). Thus, this polymer has not any interference with ferrocyanide in electrochemical investigations. Fig. 2 shows cyclic votammograms for the oxidation–reduction of the $Fe(CN)_6^{4-/3-}$ redox couple incorporated into PDMA film on the CPE electrode in the buffer solution (pH 7.00) at various scan rates. The cyclic votammograms quantitatively resemble those of solution – dissolved reactants diffusing to the electrode surface. Plots of anodic and cathodic peak currents

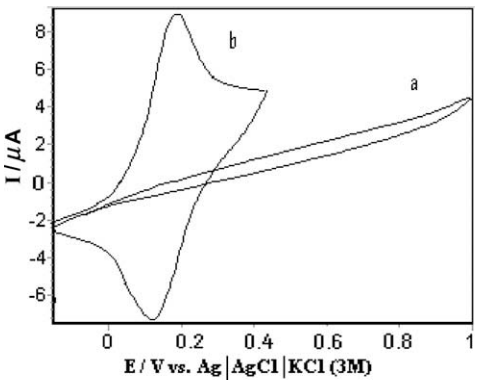

**Fig. 1.** Cyclic voltammograms of (a) PDMA and (b) PDMA/FCN film coated CPE in the phosphate buffer solution (pH 6.00). $v$ = 10 mV $s^{-1}$.

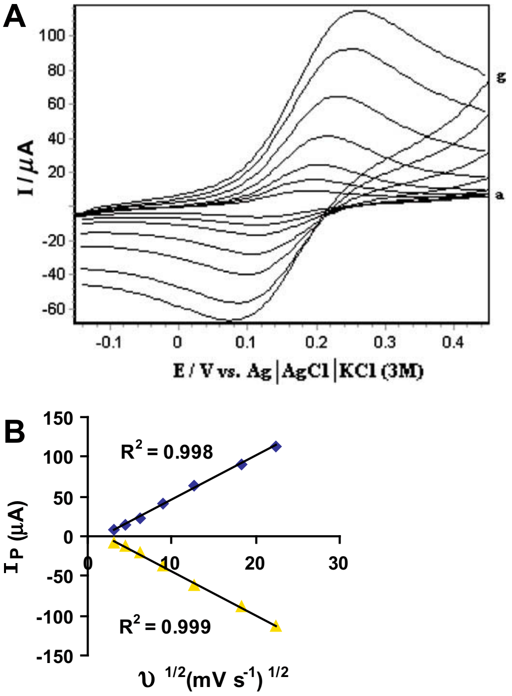

**Fig. 2.** (A) The oxidation–reduction of the $Fe(CN)_6^{4-/3-}$ redox couple incorporated into PDMA film on the CPE electrode in the phosphate buffer solution (pH 7.00) at various scan rates: (a) 10, (b) 20, (c) 40, (d) 80, (e) 160, (f) 333 and (g) 500 mV $s^{-1}$. (B) Plots of cathodic and anodic peak currents vs. $v^{1/2}$ at various scan rates.