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## Eugenol modified titanium electrode for the analysis of carbocysteine

*A eugenol immobilized electrode was developed for the assay of the carbocysteine compound. The electrochemical sensor was made by in situ electropolymerization of eugenol at titanium electrode. Cyclic voltamperometry at prepared electrode permitted to point out a reversible pattern for carbocysteine electrooxidation.*

**Key words:** *Eugenol, polymerization, modified electrode, carbocysteine, sensor*

### INTRODUCTION

Cysteine (Cys) plays an important role in several biological processes [1]; Cys or its compounds are widely used in many pharmaceutical products. Determination of Cys or its compounds is commonly used in clinical investigation, pharmaceutical industry and research.

Among many methods for determination of Cys [2,3] or its compounds, chromatographic methods are widely used. In spite of HPLC as a powerful tool [4-7], several disadvantages of HPLC in determination of Cys can be recognized. In all chromatographic methods, the sample should pass through derivatization and extraction of the reaction products before their microinjection into the column. These methods use expensive reagents and equipment, and quite long period of time for whole assay to be performed.

The present paper describes the utilization of the eugenol modified titanium electrode for electrochemical determination of Cys.

Considerable interest in conducting polymer has led to a number of important applications [8-11]. Special attention is currently being given to the preparation of new conducting electrode coatings based on composite polymers [12,13]. It is expected that this strategy will improve the behaviour of conducting polymers and will result in polymers designed for specific application. Depaoli and co-workers [14,15] described the preparation of poly(vinyl chloride) (PVC)/polypyrrole (PP) composite membranes by electropolymerizing PP inside a PVC film on the electrode surface.

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Ozata and Hirai's groups [16, 17] prepared poly (aniline)(PA)/Nafion composites by electropolymerization within pre-cast Nafion layers, while Penner and Martin [18] illustrated the advantage of Nafion-impregnated Gorotex membranes. El Mhammedi *et al.* [19] described the preparation of titanium/PP composite, by electropolymerizing pyrrole in the electrode surface.

In this report we describe a new titanium/poly-eugenol composite coating, for the determination of Cys and their derivatives.

### EXPERIMENTAL

Electrochemical experiments were performed using a Voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) guided by the general purpose electrochemical systems data processing software (Voltalab master 4 software). A conventional three-electrode system consisted of the eugenol modified working electrode, platinum counter and saturated calomel electrode (SCE) as the reference electrode.

Eugenol compound was extracted from nail cloves. All other reagents used were of analytical grade. Bidistilled water was used throughout the work, L-cysteine was purchased from Beijing Chemical Reagent Co. (China).

### RESULTS AND DISCUSSION

Electrochemical polymerization of the polymers can be carried out by potential step or potential sweep methods [20], using typical coating eugenol monomers in basic media. The cyclic voltammetric curves for the eugenol electropolymerization on titanium electrode are shown in Figs. 1 and 2. In the first cycle, a broad peak at -0.2 V (first) was observed. This peak disappears in the second cycle: this behavior indicates the rapid deposition of a non-conductive polymer onto the electrode surface. However,

when the potential scan is extended towards positive values a second peak at about 1.0 V is observed, Ciszewski *et al.* [20], in a study of the same polymerization on a glass electrode attributed the first

peak to the deposition of a polymer on the electrode surface, whereas the second peak is probably due to the phenomenon of degradation/restriction of this polymer.

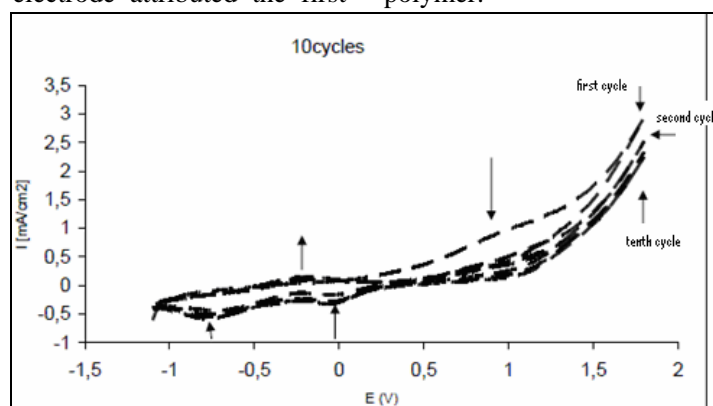


Figure 1 - Cyclic voltammograms for electrochemical polymerization of eugenol in 0.1M NaOH solution at titanium electrode scan rate: 50 mV/s

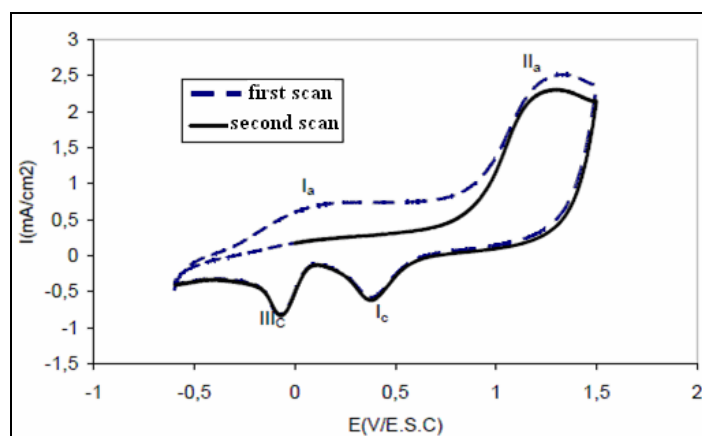
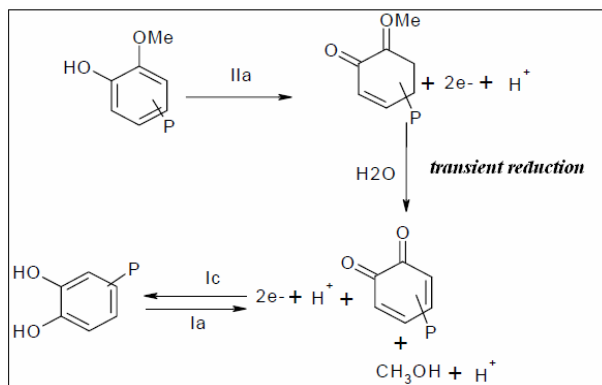


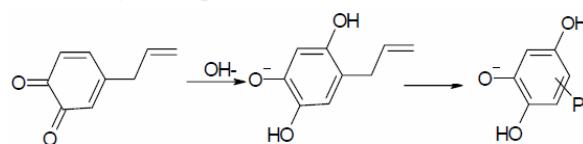
Figure 2 - Cyclic voltammograms for electrochemical polymerization of eugenol in 0.1 M NaOH solution at titanium electrode, scan rate: 10mV/s, the first and second cycles

In back scan there are two reduction peaks, at -0.07 V and 0.37V (Fig. 2). Based on the results of Petek *et al.* [21], the major reversible couple (Ia/Ic), followed by an irreversible peak IIa, can be attributed to the following steps:



where P indicates the polymeric structure in which 2-methoxy-phenol groups are stationary.

Finally, the second reduction peak IIIc is probably associated to the transition of trihydroxybenzene derivative formed during the polymerization from 4-allyl-1,2-quinone according to the reaction:



An impedance spectroscopy study was performed in order to confirm the results obtained by the cyclic voltammetry tests. Figures 3 and 4 show the impedance diagrams recorded for titanium without and with polymer respectively. In the both samples, the impedance curves are in the form of half-circle which can be attributed to the electron transfer step. The diameter of the circles increased considerably in Ti/polymer electrode, because the polymer is overoxidized at such positive potentials and becomes electrochemically inactive, which leads to the increase in the electron transfer resistance [19].

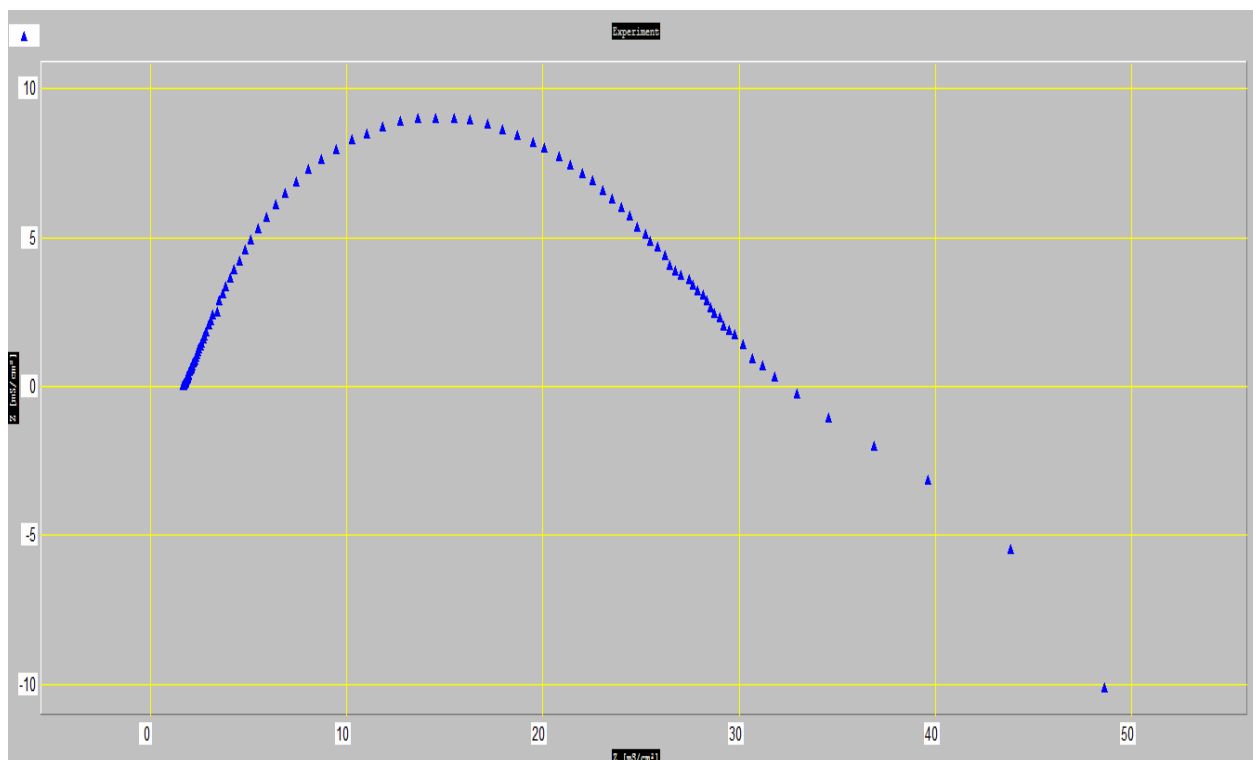


Figure 3 - Electrochemical impedance spectroscopy for Ti electrode in 0.1M  $\text{Na}_2\text{SO}_4$  solution, at open circuit potential

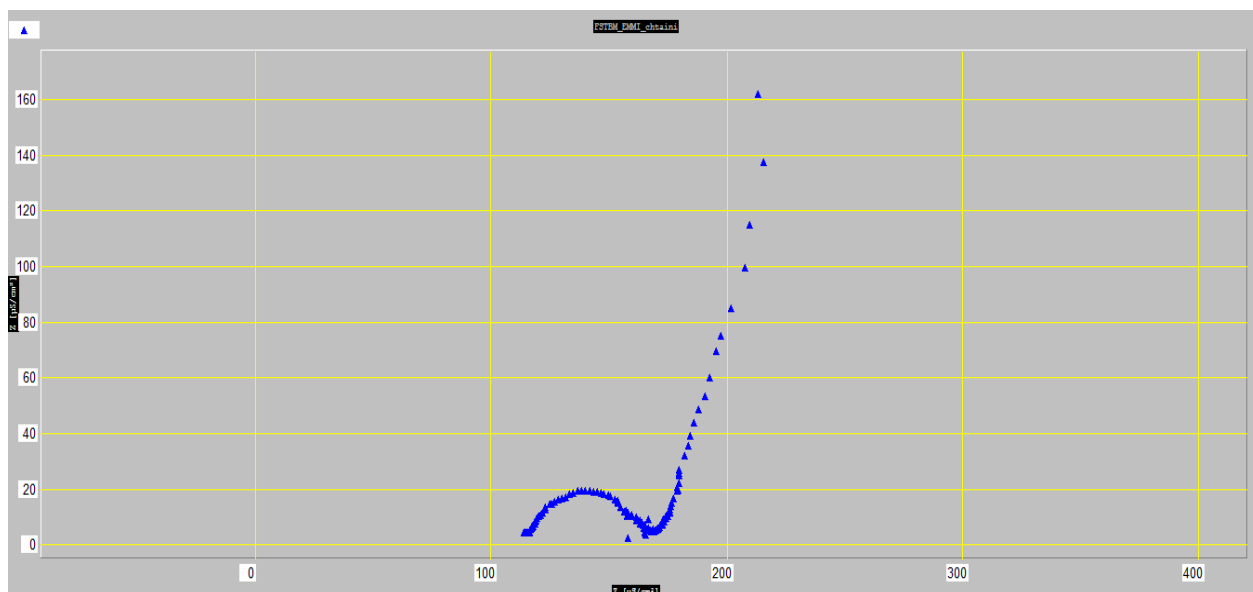
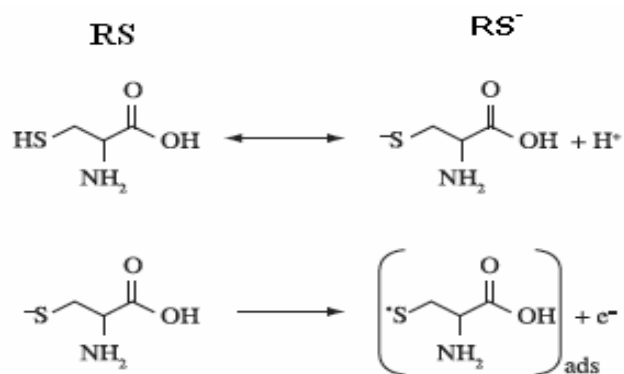


Figure 4 - Electrochemical impedance spectroscopy for Ti/polymer electrode in 0.1M  $\text{Na}_2\text{SO}_4$  solution, at open circuit potential

Figure 5 shows some of typical cyclic voltammetry curves recorded at Ti/polymer electrode after being in contact with different carbocysteine concentrations for 15 min of accumulation time. The oxidation of carbocysteine showed, in the investigated buffer media (pH 6), a well known electrochemical behavior with removal of one electron from the corresponding cation radical  $\text{RS}^{\cdot+}$  (peak, marked by arrow in Fig. 5), according to follow Scheme 1 [22].



Scheme 1 - L-cysteine oxidation mechanism at glassy carbon electrode

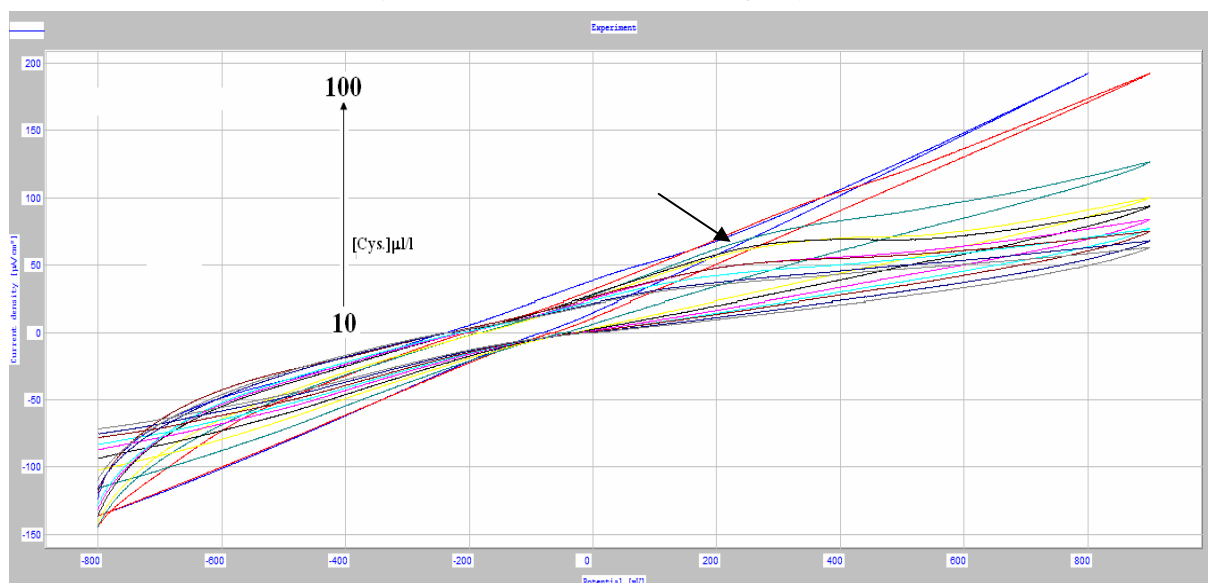


Figure 5 - Cyclic voltammograms of Ti/polymer electrode in different concentrations of carbocysteine in buffer media, pH 6

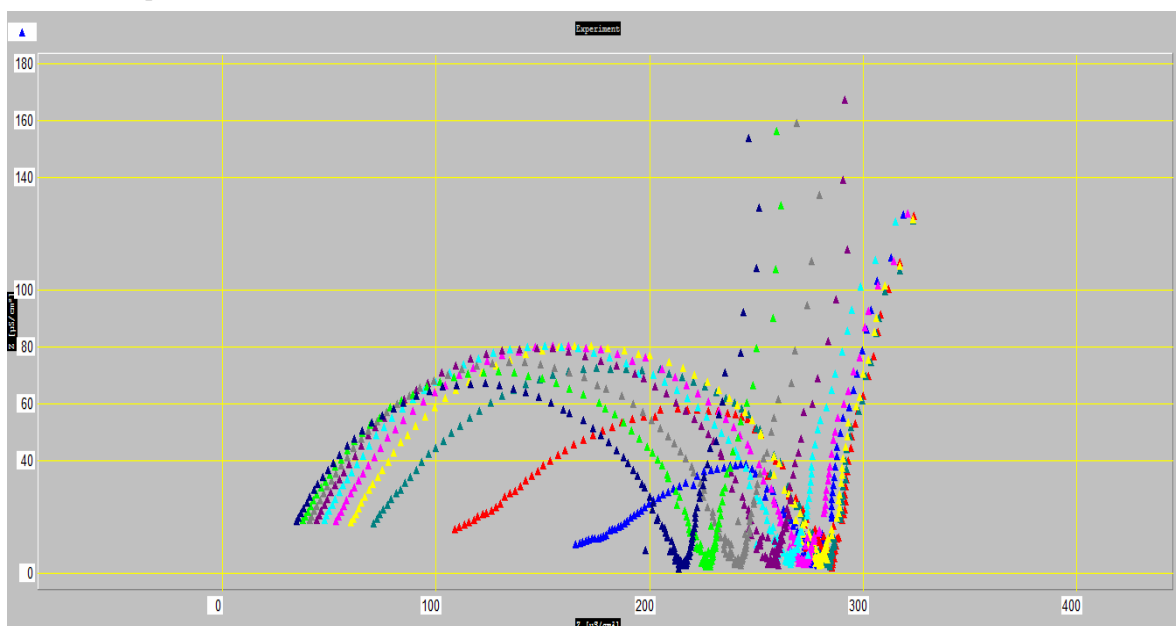


Figure 6 - Nyquist diagrams of polymer modified titanium electrode, in presence of different concentration of carbocysteine, at open circuit potential

Figure 6 shows the behavior of impedance diagrams recorded for eugenol polymer modified titanium electrode in buffer solution, in the presence of different concentrations of carbocysteine compound. We conclude that modified electrode reacts with the studied compound.

## CONCLUSION

It was demonstrated that eugenol is suitable for the preparation of an operating chemically modified electrode based on *in situ* polymerization of eugenol at titanium electrode for the detection of carbocysteine.

Initially, the results presented in this article clearly demonstrate the properties of electrochemically prepared polymer modified electrode in electrochemistry of carbocysteine.

The electrochemical behavior of carbocysteine was evaluated using the voltammetric results of modified electrode. The cyclic voltammetry showed one anodic peak associated to the oxidation of carbocysteine. The use of the polymer/Ti electrode indicates the direct analysis of the samples possible without any necessity of pre-treatments or chemical preparation stages.

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## IZVOD

### ANALIZA KARBOCISTEINA TITANSKOM ELEKTRODOM MODIFIKOVANOM EUGENOLOM

Razvijena je elektroda sa imobilisanim eugenolom za analitičko određivanje karbocisteina. Ovaj elektrohemijski senzor je dobijen *in situ* elektropolimerizacijom eugenola na elektrodi od titana. Povratna elektrooksidacija karbocisteina je registrovana na dobijenoj elektrodi cikličnom voltametrijom.

**Key words:** Eugenol, polimerizacija, modifikovana elektroda, karbocistein, senzor

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