

**ELECTROCATALYTIC OXIDATION OF ASCORBIC ACID ON CARBON PASTE  
ELECTRODE MODIFIED WITH [Ru(EDTA)(4PMC)]**

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**Abstract-** In this work the polymer 4-pyridilmethylchitosan/Ru(EDTA) ([Ru(EDTA)(4PMC)]) was used as modifier in the preparation of chemically modified carbon paste electrodes. The electrochemical behavior of the polymer compound is governed by the a conversion of the monosubstituted species for disubstituted species when the reduction of Ru<sup>III</sup> to Ru<sup>II</sup> occurs. The cyclic voltammogram of the electrode prepared with the [Ru(EDTA)(4PMC)] in the presence of ascorbic acid presented an increment in the anodic peak current in 0,38 V, which indicates that the catalysis of ascorbic acid oxidation is mediated by polymer.

**Keywords:** 4-pyridilmethylchitosan, polymer modified electrode, ascorbic acid oxidation

## INTRODUCTION

Chemically modified electrodes (CME) have attracted a great deal attention over the past decade in a wide range of potential applications in electrochemical processes, particularly in chemical analysis, catalysis reaction, ion exchange and complexation [1,2].

Ruthenium complexes are used to prepare CME due to their electrochemical reversibility [3]. Cox and Gray [4,5] successfully used a Ru-Ru(CN)<sub>6</sub> inorganic film for the oxidative detection of the insulin by flow injection analysis based on the electrocatalysis of cystein in protein. Gorki *et al.* [6] using ruthenium-oxidizing catalytic films in carbon fiber microelectrodes developed a method for the determination of insulin in physiological pH. Wang and Romere [7] used ruthenium dispersed in carbon paste enzyme electrode as a biosensor for the determination of alcohol.

Polymeric molecules have been advanced as potent modification agents in chemically modified electrodes (CME). One the most attractive aspects of polymeric coating is the preparation. Oyama and Anson [8] used polyvinylpyridine an polyacrylenitrile films as anchoring groups in the modification of pyrolytic graphite electrodes and RuEDTA complex was the redox mediator. In

recent reports [9] chitosan modified with 4-pyridinecarboxialdehyde was used to prepare carbon paste modified electrode (CPME) and tested with pentacyanoferrate(II) as electroactive species. The present works report the preparation, electrochemical and electron mediator properties of the polymer 4-pyridimethylchitosan/Ru(EDTA) [Ru(EDTA)(4PMC)] in MCPE .

#### EXPERIMENTAL

RuCl<sub>3</sub> was purchased from Aldrich Chemical Co. Other reagents used were analytical grade and used without further purification. The 4-pyridimethylchitosan (4PMC) was prepared following the procedure describe by Rodrigues et al [10].

[Ru<sup>III</sup>(EDTA)(H<sub>2</sub>O)] was prepared according to the literature [11]. The complexation of the [Ru<sup>III</sup>(EDTA)(H<sub>2</sub>O)] with 4PMC was done as follows: 0.6 g of powder the 2PMC and 4PMC was shaken in a complex solution, pH adjusted to 5 with NaOH, for 5 hours. The solid was subsequently filtered and washed with distilled water, and dried under vacuum at room temperature.

The CPME was prepared by mixing 0.4 g of electrolytic carbon powder (Fluka Co.) with 0.2 g of mineral oil (Nujol) and 0.06 g of the polymer. The paste was packed into a glass tube, which gave a geometric surface area of approximately 0.07 cm<sup>2</sup>. The electrical connection was made via a cooper wire. The surface was smoothed off by rubbing the electrode several times slowly on a soft paper surface.

Cyclic voltammograms were obtained, using a cyclic voltammeter model CV-27 (Bioanalytical Systems Inc.) coupled with an X-Y Omnigraphic 100 register (Houston Instruments). A three-electrode system was used: with a carbon paste electrode as the work electrode, a (Ag/AgCl - KCl sat.) reference electrode and a platinum wire as an auxiliary electrode.

#### RESULTS AND DISCUSSION

Cyclic voltammograms of [Ru(EDTA)(4PMC)] polymer in CPME are shown in Figure 1(2). The half-wave potential for the couple Ru<sup>III/II</sup> is -0,15 V and it is shifts to more positive values compared with that of the free complex [Ru<sup>III</sup>(EDTA)(H<sub>2</sub>O)] carbon paste electrode (1). The presence of pyridine and chitosan stabilizes the low oxidation state of the metal ion.

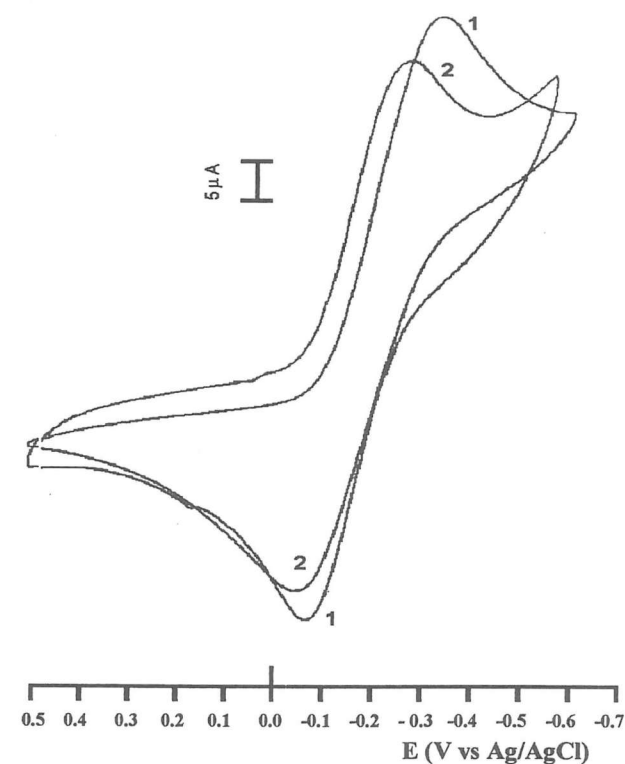


Figure 1: 1- Cyclic voltammogram of [Ru<sup>III</sup>(EDTA)(H<sub>2</sub>O)], 1 x 10<sup>-4</sup> M, in CPME. 2- [Ru<sup>III</sup>(EDTA)(4PMC)] in CPME. Electrolyte KCl 0.1M/HCl pH 2.0. Scan rates 100 mV s<sup>-1</sup>.

Figure 2 shows cyclic voltammograms of [Ru<sup>III</sup>(EDTA)(4PMC)] at CPME pre-conditioned in -0.45V. The voltammograms presents two distinct redox centers. The peak in -0.15V is attributed to the Ru<sup>III/II</sup> redox couple of the one-pyridine to complex of RuEDTA. The second peak in 0.25V represent couple Ru<sup>III/II</sup> coordinated to two-pyridine group in the RuEDTA complex. Figure 2 shows an increase in the intensity of peak current for disubstituted species. Simultaneously, a decrease of the intensity of peak current takes place for the monosubstituted species.

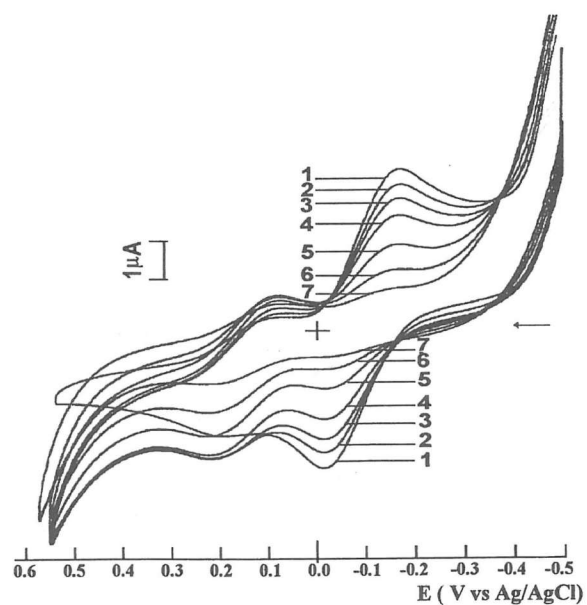


Figure 2: Cyclic voltammogram of  $[Ru^{III}(EDTA)(4PMC)]$  in CPME. Before each voltammogram the electrode was conditioned at  $-0.45$  V at time indicate (minute): 1-1; 2-3; 4-6; 5-11; 6-17; 7-25. Electrolyte KCl 0.1M/HCl pH 2.0. Scan rate  $100\text{ mV}\cdot\text{s}^{-1}$ .

The original voltammogram can be restored by maintaining the electrode at a positive potential ( $0.6$  V) for 10 minutes.

The failure of  $Ru^{III}EDTA$  to accept more than one pyridine ligand is in agreement with the weakness  $\pi$  basicity of  $Ru^{III}$  [12]. The conversion of monopyridine to dipyrindine polymers is represented in the scheme below.

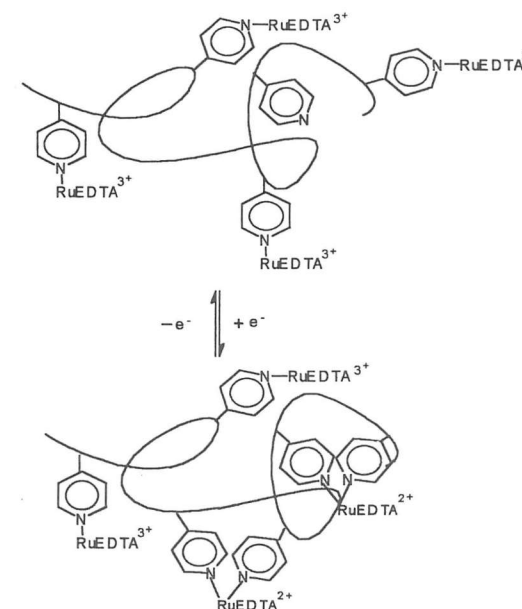


Figure 3: Schema of interconversion of the  $[Ru^{III}(EDTA)(4PMC)]$  for  $[Ru^{II}(EDTA)(4PMC)_2]$ . The second coordinated pyridine group probably displaces a coordinated carboxyl group from the  $Ru^{III}$  center.

### Electron Mediator Property

Modified electrode has been used for the development of analytical methods for ascorbic acid determination [13]. This study was extended for the  $[Ru(EDTA)(4PMC)]$  electrode in order to evaluate its ability to mediate the electrocatalytic oxidation of ascorbic acid.

A cyclic voltammogram for CPME exhibits four redox peaks Figure 4(1). In the presence of ascorbic acid an increase in the anodic current of the electrode is observed as at  $0.38$  V assigned to the reduction of  $Ru^{III}$  with two pyridine group, Figure 4(3). The anodic current generated in the region of oxidation potential of reduced forms of the mediator illustrated the catalysis of ascorbic

acid oxidation via mediator. In contrast, after with modified the oxidation of ascorbic acid on a carbon paste electrode proceeds at potential higher than 0.9 V, Figure 3(2).

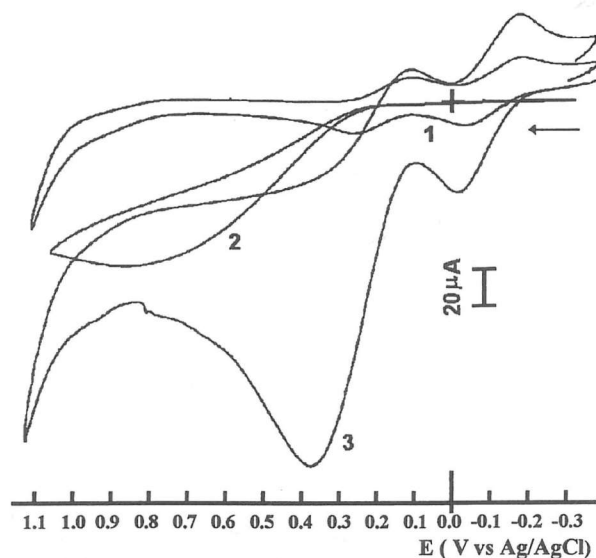


Figure 4: Cyclic voltammogram of  $[\text{Ru}^{\text{II}}(\text{EDTA})(4\text{PMC})]$  in CPME: (1) absence of ascorbic acid, (3) presence of ascorbic acid, (2) cyclic voltammogram of ascorbic acid in carbon paste electrode. Determination conditions: ascorbic acid concentration  $1.0 \times 10^{-4}$  M; Electrolyte KCl 0.1 M/pH 2.0. Scan rates  $100 \text{ mV s}^{-1}$ . The current value was read 60 seconds after addition of the ascorbic acid.

## CONCLUSION

In conclusion, the results of electrocatalytic oxidation of ascorbic acid on CPME indicate that  $[\text{Ru}^{\text{III}}(\text{EDTA})(4\text{PMC})]$  can be used to manufacture a chemical sensor for ascorbic acid determination. More experiments are required for application CPME as an amperometric detector in liquid chromatography and flow-injection analyses.

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Received, December 22, 1999  
Revised, March 24, 2000