

Electrochemical Synthesis of Poly(pyrrole-co-[Cu(salabza)]): its Electrocatalytic Activity Towards the Oxidation of Catechol

Poli(Pirol-ko-[Cu(salabza)])'nin Elektrokimyasal Sentezi: Katekolün Oksidasyonunda Elektrokatalitik Aktivitesi

Research Article

Süleyman Yalçinkaya*, Didem Çakmak

Mustafa Kemal University, Department of Chemistry, Hatay, Turkey.

ABSTRACT

This paper presents the study of the electrochemical synthesis of poly(pyrrole-co-[Cu(salabza)]) and its application to the electrocatalytic oxidation of catechol. The synthesis has been achieved by cyclic voltammetry (CV) technique on the platinum electrode in non-aqueous acetonitrile solution. The characterization of the copolymer was done by using FT-IR, UV-vis, CV, Scanning Electron Microscopy (SEM), TG-DTA techniques. The SEM micrographs clearly indicate that the copolymer film has different structure from [Cu(salabza)] and polypyrrole films. Moreover, electrochemical studies show that the copolymer film has good stability and electro activity. As well, the electrocatalytic studies show that the copolymer coating exhibited catalytic activity towards the oxidation of catechol.

Key Words

Copolymer, schiff base metal complexes, electrochemical techniques, catalytic activity.

ÖZ

Bu makale, poli(pirol-ko-[Cu(salabza)]) kopolimerinin elektrokimyasal sentezini ve onun katekol elektro katalitik oksidasyonu üzerindeki uygulamasını içermektedir. Sentez işlemi platin elektrot yüzeyine susuz ortamda asetoneitril çözeltisinde dönüşümlü voltametri tekniği ile gerçekleştirilmiştir. Kopolimerin karakterizasyonu FT-IR, UV-vis, CV, taramalı elektron mikroskopu (SEM), TG-DTA teknikleri kullanılarak yapılmıştır. SEM görüntüleri kopolimer filminin, [Cu(salabza)] ve polipirol filmlerinden farklı bir yapıya sahip olduğunu açıkça göstermektedir. Bunun yanı sıra elektrokimyasal çalışmalar kopolimer filminin kararlılığının ve elektro aktivitesinin iyi olduğunu göstermiştir. Elektro katalitik çalışmalar kopolimer kaplamanın katekol oksidasyonu için katalitik aktiviteye de sahip olduğunu göstermiştir.

Anahtar Kelimeler

Kopolimer, schiff bazı metal kompleksleri, elektrokimyasal teknikler, katalitik aktivite.

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Correspondence to: S. Yalçinkaya, Mustafa Kemal University, Faculty of Arts and Sciences, Department of Chemistry, Hatay, Turkey.

Tel: +90 326 245 5840

Fax: +90 326 245 5867

E-Mail: suleyman1444@hotmail.com

INTRODUCTION

Conducting polymer films have a wide variety of applications in many fields including electroanalysis, electrocatalysis, biosensors and corrosion protection [1-8]. These films have been generally produced by electrochemical way. Electropolymerization allows uniform coating on irregular surfaces and easy electrochemical control of the film thickness. Polypyrrole has long been marked as one of the most promising polymers in conducting polymers family due to its good conductivity and ease of synthesis. Polypyrrole can be also easily produced as a film on the metal surface by the electrochemical method [9]. Furthermore, it was reported that the electrochemical polymerization of pyrrole is convenient for carrying out the coating of electrode surfaces by non-passivating polymer films containing active centres, especially transition metal complexes. However, polypyrrole film has low mechanical and thermal properties. The copolymerization has long been utilized to improve various properties (conductivity, thermal and electrochemical stability, mechanical properties and porosity etc.) of the polymer films [10,11].

Schiff bases metal complexes are a class of compounds that have been studied extensively because of their chemical and physical attractive properties, and their wide range of applications in various scientific areas, such as electrocatalysis, sensors and electrochromic displays [12-17]. In recent years, the electropolymerization of various metal-salen complexes have been investigated. Researchers have incorporated Schiff base complexes into polymers, generating new materials with useful mechanical, thermal, chemical and electronic properties. There are a few studies concern with incorporated Schiff base complexes into conducting polymers in the literature [18]. One of these reports has been studied by Chierito et.al. who have achieved polypyrrole iron(II) Schiff-base complex film on the glassy-carbon disc electrode by electrochemical method [19].

Catechol is dihydroxybenzene compound widely used in the pharmaceuticals, cosmetics, dyes, foods and so on [20-22]. On the other hand,

catechol is considered as environmental pollutant because of its low degradability and high toxicity in the environment [23]. Several techniques have been established for quantitative detection of catechol in environmental samples such as spectrophotometry [24], fluorescence [25], and electrochemical methods [26]. Electrochemical methods are fairly applicable for catechol detection due to its electrochemically active nature. At the same time it provides advantages over the other techniques, including low cost, simple instrumentation, fast response; high sensitivity, selectivity, stability and also improvable with new electrode modification methods.

In this study, we aimed to prepare a copolymer with pyrrole and metal complex with high thermal stability and electrochemical properties which can be used as alternative material in sensor and catalytic applications. For this purpose, poly(pyrrole-co-[Cu(salabza)]) coatings were synthesized electrochemically by using cyclic voltammetry technique. The synthesized copolymer film was characterized via cyclic voltammetry, FT-IR, UV-vis techniques. Besides, surface morphology of the copolymer film was also examined by SEM micrographs; the thermal behavior of the copolymer film was tested by using TGA and DTA measurements. In addition, electrocatalytic activity of modified electrode was tested for catechol oxidation.

MATERIALS and METHOD

Pyrrole (Merck) was distilled first and, acetonitrile (Merck) and LiClO_4 (Fluka) were used as customary conditions. $\text{Cu}(\text{N,N}'\text{-bis(salicylidene)-2-aminobenzylamine})$ was prepared using acetate ion of $\text{Cu}(\text{II})$ and $\text{N,N}'\text{-bis(salicylidene)-2-aminobenzylamine}$ (salabza) as described previously (Figure 1) [27].

The electrochemical synthesis of the copolymer film was carried out using cyclic voltammetry technique, in 0.01 M pyrrole and 0.01 M metal complex containing solution of 0.15 M LiClO_4 in acetonitrile. All the electrochemical studies were carried out in a conventional three electrode set up, open to the atmosphere, by using $\text{CHI}_6\text{O}_4\text{E}$ model

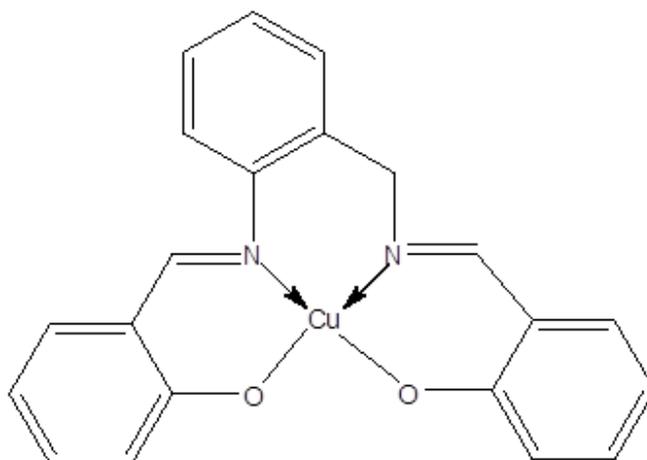


Figure 1. The structural representation of [Cu(salabza)].

electrochemical analyzer. The counter and working electrodes were platinum foil with 2 cm² surface area and Ag/AgCl electrode was used as a reference and all the potential values referred to this electrode. The Fourier transformed infra-red (FT-IR) spectroscopic measurements were realized for the copolymer film. The pellets (KBr-pressed) were prepared and the measurements were conducted with a Perkin Elmer spectrum RX1 FT-IR system instrument. The characterization of the copolymer film in ultraviolet-visible (UV-Vis) region was also examined with a Perkin Elmer Lambda 25 UV-Vis spectrophotometer. For this purpose, the composite film was dissolved in dimethyl sulfoxide (DMSO). The morphology of the composite film was also illuminated with Scanning Electron Microscopy (SEM) technique. Moreover, TGA measurements were performed at a heating rate 10 °C/min with a sample size of 5 mg in nitrogen atmosphere. Phosphate buffer solution (pH 7) was used as supporting electrolyte for electrocatalytic investigation studies. Stock solution of catechol (1 mM) was prepared by dissolving in water. The calibration plot for catechol was obtained by standard addition of 1 mM catechol.

RESULTS and DISCUSSION

Synthesis

The successive voltammograms recorded for Pt electrode in [Cu(salabza)] (a), pyrrole (b) and pyrrole + Cu[(salabza)] (c) containing solutions are given in Figure 2. The cyclic voltammetry result obtained for poly[pyrrole-co- Cu(salabza)] coating system has different properties from CVs of

polypyrrole and [Cu(salabza)]. The voltammogram of [Cu(salabza)] shows oxidation and reduction peak at the subsequent cycle (Figure 2a). The monomer oxidation process was found to start at around 0.8 V. The current density associated to monomer oxidation increased at first four cycles, but, decreased after the following cycle. It can be explained with the film formation of [Cu(salabza)] that slowly covers the electrode surface. Continued scanning also led to an increase in current of reduction peak (between a range of -0.2 and +1.0 V) response consistent with [Cu(salabza)] film formation that fully covered the electrode surface [27]. Figure 2b. shows the CVs recorded during the polypyrrole film growth on the platinum electrode in non-aqueous acetonitrile solution. The monomer oxidation process of pyrrole was found to start at around 0.8 V. During the successive CVs applied for film growth (for increasing the thickness), the oxidation-reduction process of produced polypyrrole film was observed as anodic and cathodic waves between a range of -0.2 and +1.0 V, in the forward and reverse scans. It must be noted that the current values constantly increase with the following scan cycles (Figure 2b). This can be explained by catalytic behavior of the polypyrrole film on polymerization [28]. Figure 2c. indicates the CVs recorded for during the poly[pyrrole-co-Cu(salabza)] film growth on the platinum electrode. The potential range applied for the film growth of the copolymer was between -0.2 and +2.0 V. The copolymer formation process was found to start at around +1.0 V. Besides, the oxidation and reduction peaks (between -0.2 and +1.0 V) of the copolymer film (similar to the

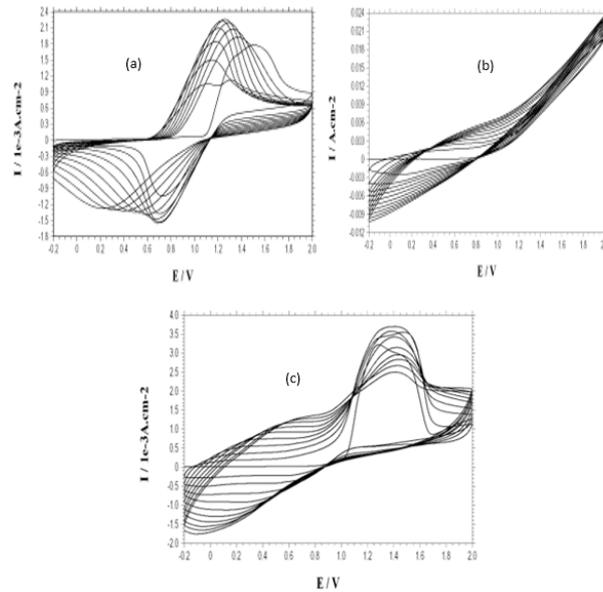


Figure 2. The voltammograms recorded for during the [Cu(salabza)] (a), polypyrrole(b) and poly(pyrrole-co-[Cu(salabza)]) (c) film growth on platinum electrode in non-aqueous acetonitrile solution, scan rate; 50 mV/s.

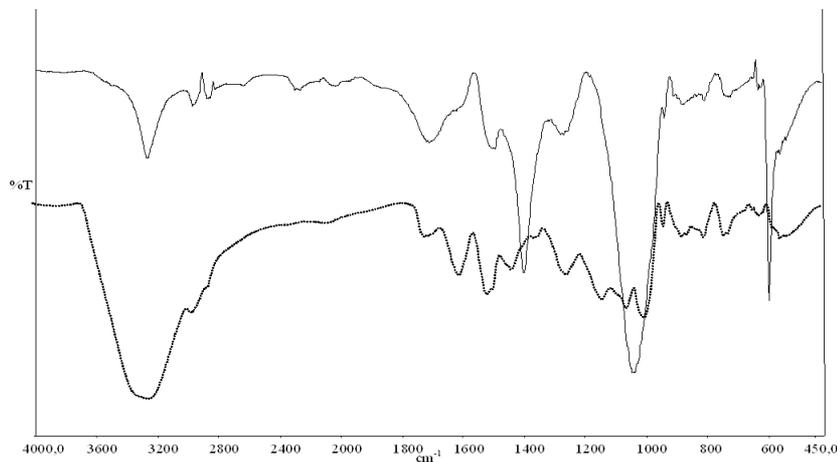


Figure 3. FT-IR spectra of polypyrrole (—) and poly(pyrrole-co-[Cu(salabza)]) (----).

polypyrrole CVs), due to transitions between its oxidation and reduction states, were clearly seen in this voltammogram (Figure 2c). As a result of these studies, a homogeneous copolymer film was obtained on the metal surface.

Solubility

The solubility of the copolymer film was investigated in various organic solvents such as DMSO (dimethylsulfoxide), DMF (dimethylformamide), chloroform, acetone, NMP (N-methylpyrrolidone) and THF (tetrahydrofuran) at room temperature. Copolymer films (2 mg) were put in 2 ml of organic solvents and the mixtures were treated in ultrasonic

bath for 24 h. The result of the solubility studies showed that DMSO was the best solvent for the copolymer film than the others.

FT-IR Spectra Results

FT-IR spectra results of polypyrrole, poly[Cu(salabza)] and poly(pyrrole-co-[Cu(salabza)]) are given in Figure 3. In the FT-IR spectrum of polypyrrole, the peak at 3275 cm⁻¹ can be attributed to the typical N-H stretching vibration. The characteristic peaks at 1570 cm⁻¹ and 1420 cm⁻¹ correspond to the C=C stretching of pyrrole ring [29]. In addition, the peaks at 1300 cm⁻¹ and 1050 cm⁻¹ were caused by C-N and C-H stretching vibrations of the pyrrole

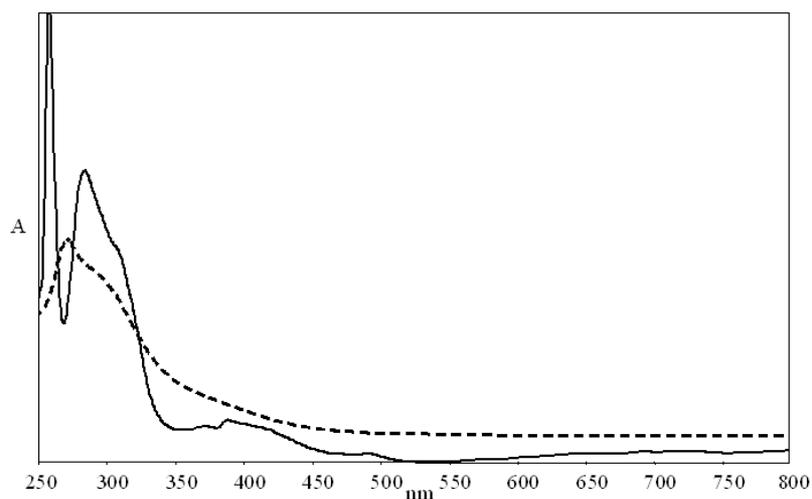


Figure 4. UV-vis spectra of polypyrrole (---) and poly(pyrrole-co-[Cu(salabza)]) (—).

units, respectively [30]. As a different from the FT-IR spectrum of polypyrrole, in the spectrum of poly(pyrrole-co-[Cu(salabza)]) a broad band was observed at around 3300 cm^{-1} attributed to the overlapping of N-H stretching of pyrrole rings and O-H vibrations of hydrated water molecules on the metal centre of the Schiff base complex units. The most important evidence supporting the formation of copolymer, involving Schiff base complex ([Cu(salabza)]), is the significant peak that was observed around 1600 cm^{-1} attributed to the C=N group of Schiff base moieties in the spectrum of the copolymer [31]. Furthermore, more vibrational modes were observed due to the introducing of [Cu(salabza)] units in the polymer skeleton, for example, the peaks at 1170 cm^{-1} and 590 cm^{-1} can be assigned to C-O and Cu-O bonds, respectively.

UV-vis Spectra Results

The ultraviolet-visible (UV-vis) spectra of polypyrrole and poly(pyrrole-co-[Cu(salabza)]) were recorded in DMSO solvent (Figure 4). The UV-vis spectra of poly-pyrrole and poly(pyrrole-co-[Cu(salabza)]) are different from each other. The characteristic bands of polypyrrole are observed at 270 nm and 300 nm as $\pi-\pi^*$ transitions for C=C and C=N groups, respectively [32]. As main difference from polypyrrole, in the spectrum of poly(pyrrole-co-[Cu(salabza)]) new absorption bands were observed at 350-510 nm regions. There are two important bands observed in that region as charge-transfer (MLCT) transition from

the $p-\sigma$ orbitals of the donor atoms to d orbitals of the copper ion in the range of 370-430 nm and d-d transitions of the Cu(II) ion in the complex units at 480-510 nm region. Also a new intense band was observed at 260 nm is attributable to the $\pi-\pi^*$ transitions of the aromatic C=C bonds of the Schiff base (salabza) moieties [33]. On the other hand, the sharp peak and the shoulder (similar shape in the poly-pyrrole spectrum) at the range of 270-340 nm observed in the spectrum of poly(pyrrole-co-[Cu(salabza)]) can give a good evidence for the presence of the pyrrole units in the copolymer skeleton. The shifting in the absorption bands of these transitions can be explained by the coupling of the pyrrole units with the Cu(salabza) units in the copolymer structure.

Morphology

The SEM micrographs of [Cu(salabza)] and the copolymer films are given in Figure 5. It was evident that the synthesized copolymer films had a significantly different structure from [Cu(salabza)] film. These differences can be attributed to formation of the copolymer. The copolymer film deposited without defect or crack on the surface. Besides, the SEM micrograph shows clearly that the surface of the copolymer coating was granular or sprout-like in nature.

The images of [Cu(salabza)] and the copolymer film are given in Figure 6. Visual inspection of the electrode surfaces showed the deposition of a blue-yellow film [Cu(salabza)] and dark bluish

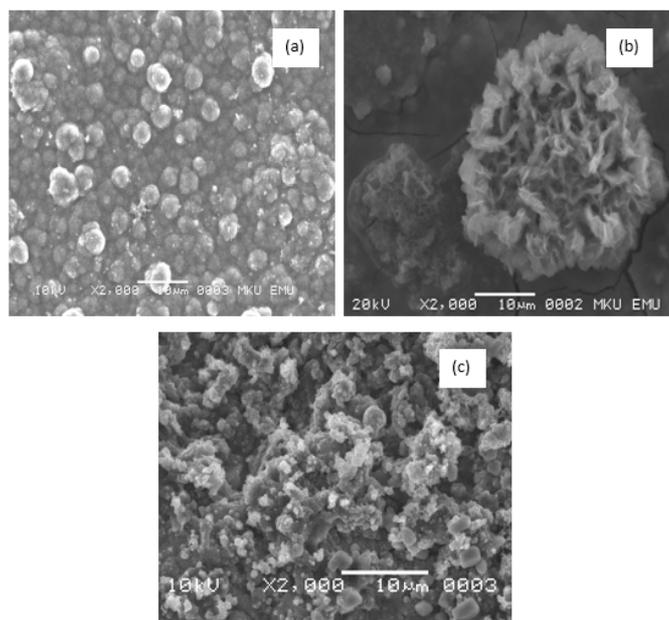


Figure 5. The SEM micrographs of polypyrrole (a), [Cu(salabza)] film (b) and poly (pyrrole-co-[Cu(salabza)]) (c).

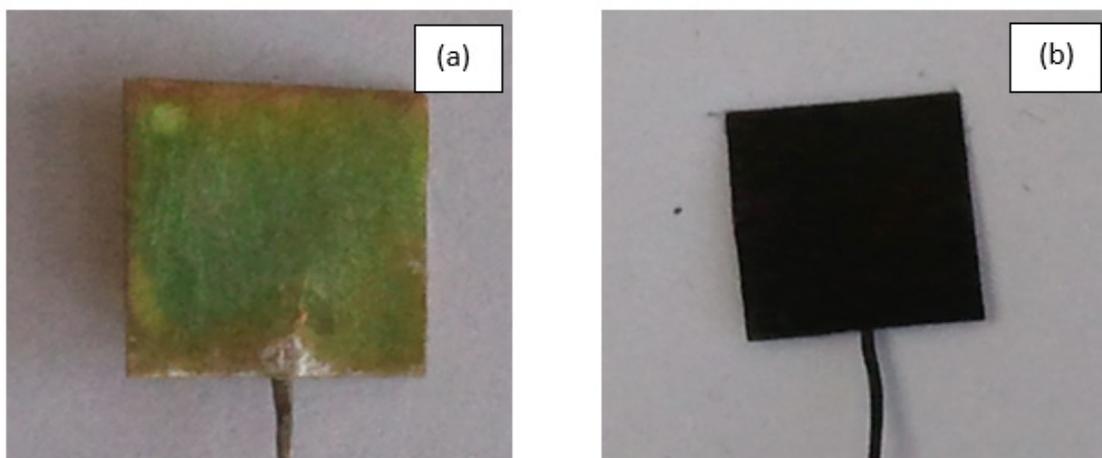


Figure 6. The images of [Cu(salabza)] film (a) and poly(pyrrole-co-[Cu(salabza)]) (b).

black film (copolymer). It can be concluded that the coloration differences of these films supported the copolymer formation.

As a result of the characterization studies, the proposed structure of the copolymer is given in Figure 7 [34].

Electrochemical Behavior

In order to examine the stability and electroactivity of the copolymer which was synthesized on the Pt electrode, the successive cycles were recorded in 0.1 M KCl solution (Figure 8). The oxidation of polymer film was observed in the forward scan

and the reduction was realized at the reverse scan. The current density values involved during these successive cycles were informative about the aspect of polymer film's electroactivity and degradability [35]. It was clearly seen that the copolymer coating had high and stable current values during the successive cycles. The copolymer film did not show degradation between oxidation and reduction states.

Thermogravimetric Analysis

The thermal behavior of poly(pyrrole-co-[Cu(salabza)]) was investigated by TG-DTA under nitrogen atmosphere. The TG-DTA curve of

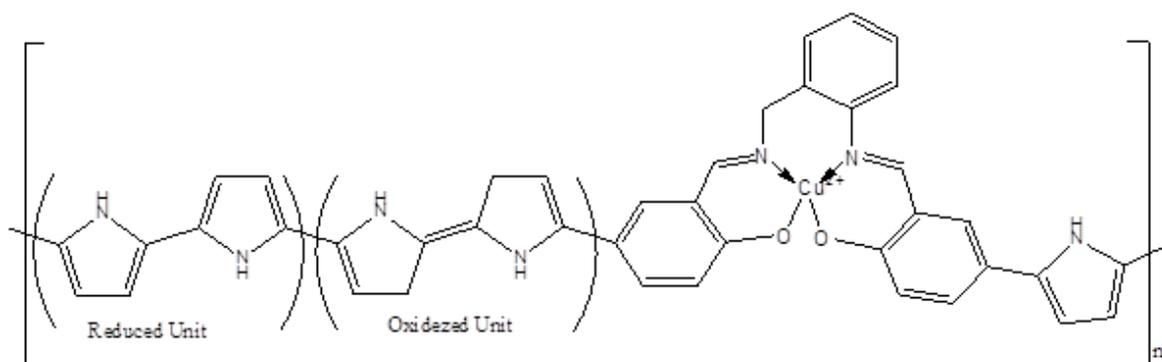


Figure 7. The structural representation of poly (pyrrole-co-[Cu(salabza)]).

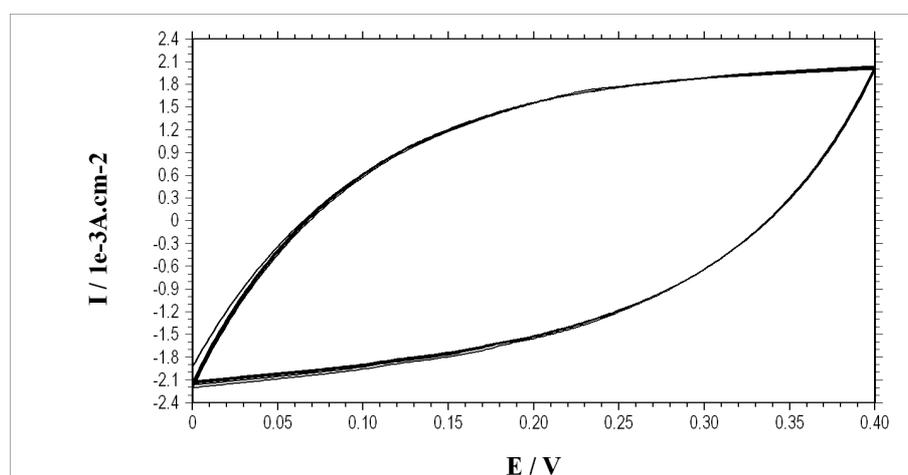


Figure 8. Successive CVs recorded for poly (pyrrole-co-[Cu(salabza)]) coated sample on the Pt electrode in 0.1 M KCl, scan rate; 50 mV/s.

poly(pyrrole-co-[Cu(salabza)]) was given in Figure 9. It was clearly seen that there were two main mass loss stages as endothermic process at a range of 70-210°C and 300-420°C. The first stage can be attributed to the water hydration and dopant (counter ions) ClO_4^- elimination and the second one might correspond to the degradation parts elimination. In addition to these endothermic process there were also two exothermic processes observed at the range of 210-300°C and 420-550°C. The first exothermic stage might be due to the thermal decomposition and chemical modification of the polymer skeleton. The second process can be assigned to the decomposition and metal oxide formation.

The electrochemical oxidation of catechol

Electrocatalytic effect of the modified platinum electrodes was investigated by cyclic voltammetry (Figure 10). The electrochemical response of

catechol at unmodified platinum electrode and at modified electrode with poly(pyrrole-co-[Cu(salabza)]) film was studied in pH 7 phosphate buffer solution from -0.2 to 0.8 V vs. Ag/AgCl potential range with 50 mV s⁻¹ of scan rate. A significant increase in the oxidation peak current of catechol at modified electrode was observed when compared with the unmodified platinum electrode in phosphate buffer solution medium. Copolymer coated electrode exhibits catalytic activity towards the oxidation of catechol but metal complex coated electrode has not shown, which is probably related to the close proximity of the pyrrole unit-metal centre interaction in the electropolymerized film.

Square wave voltammetry (SWV) is used for investigation of correlation catechol oxidation peak current-concentration change by using the copolymer coated electrode.

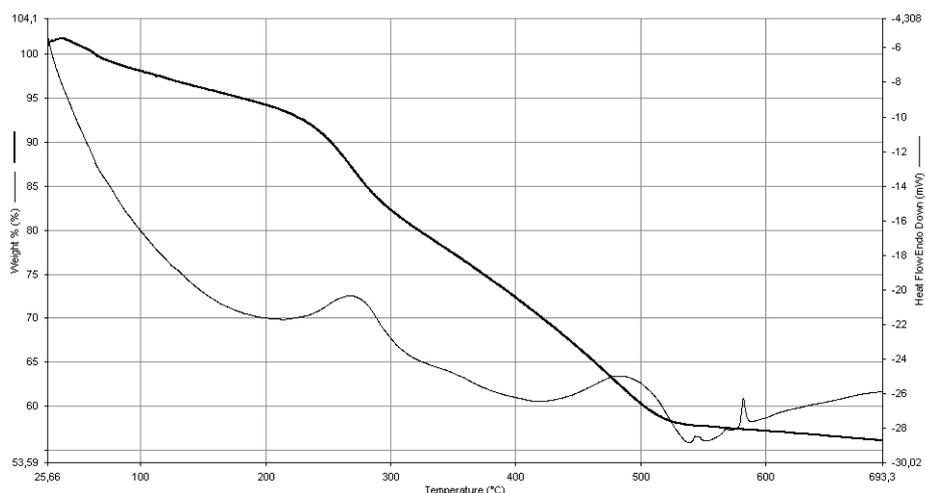


Figure 9. The images of [Cu(salabza)] film (a) and poly(pyrrole-co-[Cu(salabza)]) (b).

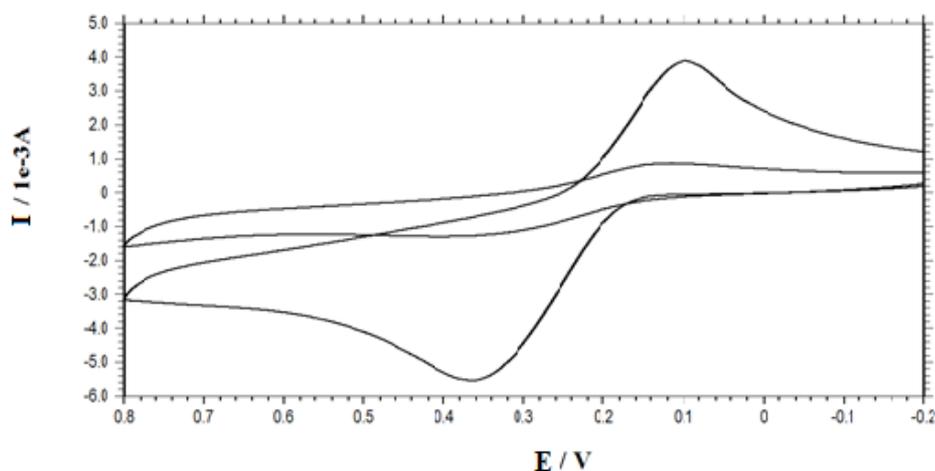


Figure 10. Electrooxidation CVs of bare Pt and Copolymer-Pt electrode in pH= 7 Phosphate buffer solution added 1×10^{-3} M Catechol. scan rate was 50 mV/s.

Figure 11 shows a series of SWVs of catechol in pH= 7 phosphate buffer solution. The peak current for catechol oxidation increased linearly with the increasing of concentration in the range of 0.11-0.70 μ M with a correlation coefficient $R = 0.9985$. At higher catechol concentration than 10^{-7} M the peak current deviated from the straight line. The detection limit was calculated as 0.4×10^{-7} M for catechol ($S/N=3$) (Table 1).

Also selectivity of modified electrode was studied in the presence of some common ions (Na^+ , Cl^- , Zn^{2+} , SO_4^{2-} , Ca^{2+} , K^+ , Mg^{2+} , NO_3^-) for the catechol electrooxidation in buffer solution (pH= 7) medium. The results showed that 100 fold excess of ions has no effect on the peak currents for the oxidation of catechol.

CONCLUSIONS

Poly(pyrrole-co-[Cu(salabza)]) film has been electrochemically synthesized by cyclic voltammetry technique in dissolved 0.15 M LiClO_4 acetonitrile solution. The copolymer film has been characterized using FT-IR, UV-vis, Cyclic Voltammetry, SEM, Photographs and TG-DTA techniques. The SEM micrograph of the copolymer film showed that the copolymer film covered on the platinum electrode without defects or cracks. Also, from the results of the electrochemical studies, it can be easily stated that the copolymer film has high thermal stability and electroactivity. Although metal complex coated electrode has not shown catalytic activity, the copolymer coated electrode exhibits catalytic activity towards the oxidation of

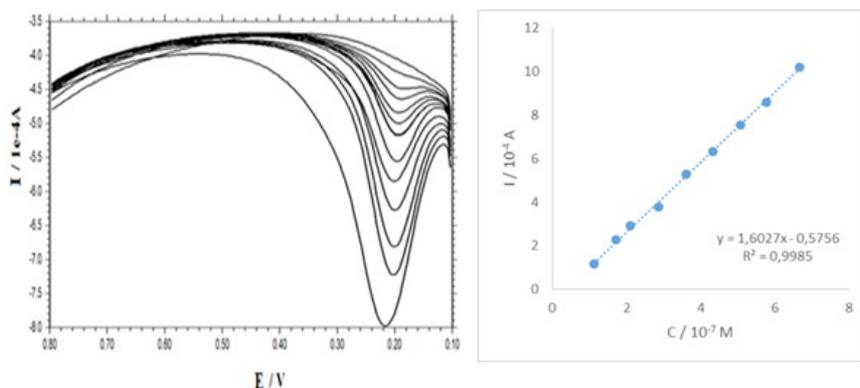


Figure 11. SWVs and calibration plot for various concentrations of catechol at copolymer-Pt electrode in pH=7 Phosphate buffer solution. scan rate was 50 mV/s.

Table 1. Comparison of proposed modified electrode with different modified electrodes for Catechol determination.

Modified electrode Materials	Working concentration of Catechol ($\mu\text{mol L}^{-1}$)	Detection Limits ($\mu\text{mol L}^{-1}$)	Reference Nos.
Sol-Gel/Au Composite (Tyr)	1.0-6.0	0.30	[36]
Polypyrrole microfibers (Tyr)	1.0-400	0.02	[37]
Poly (aniline-co-o-p-aminophenol)(Pt)	5.0-500	0.80	[38]
GO-Terthiophen-CNT	0.01-200	0.012	[39]
poly(pyrrole-co-[Cu(salicylate)])	0.11-0.70	0.04	This work

Tyr: Tyrosinase; **GO:** Graphen oxide; **CNT:** carbon nanotube

catechol. We have concluded that the high thermal stability and good electroactivity of synthesized copolymer film is promising for many application areas.

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