

Electropolymerization and characterization of salophen derivative Schiff base Co(II) and Ni(II) complexes on the graphite electrode and electrocatalytic investigations

D. Cakmak^{1*}, T. Bulut

¹Department of Chemistry, Faculty of Arts and Sciences, Mustafa Kemal University, 31040, Hatay, TURKEY

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In this study, pencil graphite electrode surfaces were modified with Salophen derivative Schiff base Co(II) and Ni(II) complexes. Surface modification procedure was carried out by electrochemical oxidation method at 0.0-2.0 V potential range in acetonitrile containing 0.15 M LiClO₄ as a supporting electrolyte medium. The prepared modified surfaces were characterized by cyclic voltammetry, EIS, FT-IR UV-Vis and SEM/SEM-EDX techniques. Modification of surfaces was confirmed by results of characterization studies. The electrocatalytic activity of modified electrodes was investigated upon bioanalytical species like ascorbic acid, catechol, cysteine etc. It was seen that both modified electrodes showed excellent electrocatalytic activity on catechol, but the catalytic activity potential of the electrode modified with Co (II) complex was higher on the other species.

Keywords: Schiff Base metal complex, electropolymerization, surface characterization, electrocatalytic investigation.

INTRODUCTION

Schiff bases are compounds that were first used as a ligand by Schiff in 1864. Schiff bases and its metal complexes are still being worked on remarkably in recent years because they have antibacterial, antiviral, anticancer and antifungicide properties as well as a wide variety of applications in different fields such as chemical analysis, catalytic systems, pesticide structures, oxygen transmission and sensor systems [11, 12]. Schiff bases, and especially its metal complexes, are attracting attention as modifying materials because of their stable and easily synthesizable structures, since they allow the functional groups to be varied in surface modification studies [13]. In recent years, development of new working electrode materials prepared by electropolymerization of Schiff metal complexes by electrochemical methods have been attracting considerable attention and also the determination of electrocatalytic activities on different types of analytes and the development of new analytical methods by using of these modified electrodes [14-15]. With the appropriate modification materials, new working electrode surfaces can be prepared and rapid, selective and sensitive determination of species are possible as electrochemically [16-19].

This study was concerned with the preparation

of modified electrodes with electropolymerization of Schiff base metal complex onto pencil Graphite electrode and also investigation of electrocatalytic activity of these electrodes. Characterization of modified electrodes was realized with electrochemical, spectroscopic and microscopic techniques.

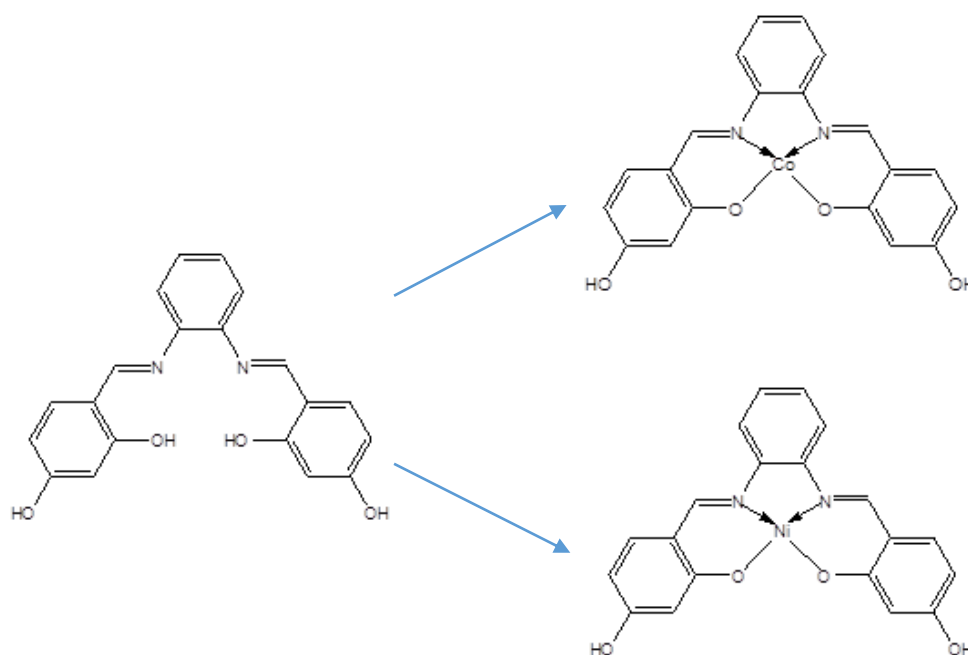
EXPERIMENTAL

Materials and methods

Electropolymerization studies of Schiff base metal complexes were performed by using of conventional three electrode system and a CHI 604E model electrochemical analyzer for cyclic voltammetry (CV) measurements. All the electrochemical studies were carried out by using a pencil graphite (GFE), Pt wire and saturated Ag/AgCl (3 M NaCl) were used as working, counter and reference electrodes, respectively. The outer surface of the graphite pencil electrode was covered with polyester for the purpose of controlling the surface area in electrochemical studies and polishing device (Polisher) was used for cleaning of working electrodes.

Schiff base [H₂L] and metal complexes ([CoL], [NiL]) were synthesized according to the literature [20]. The proposed structures of [H₂L], [CoL] and [NiL] are given below.

* To whom all correspondence should be sent.
E-mail: didem.deleti@gmail.com, dcakmak@mku.edu.tr



Proposed structure of H_2L , $[CoL]$ and $[NiL]$.

Modification procedure was performed by CV with scanning from 0.0 to 2.0 V at a sweep rate of 50 mV s^{-1} for 25 cycles in 1 mM $[CoL]$ and 1 mM $[NiL]$ solutions in acetonitrile containing 0.15 M $LiClO_4$.

Stability of modified surfaces CoL -GFE, NiL -GFE was tested by CV method using sequential potential scans in a 0.3 M KCl support electrolyte medium. The CV method has also been used for the electrochemical characterization of modified surfaces by using of redox probes (ferrocene, ferricyanide). The 1.10^{-3} M ferrocene solution was prepared in an acetonitrile containing 0.1 M $LiClO_4$. Ferricyanide test was carried out in 0.1 M KCl solution containing 1.10^{-3} M $K_3[Fe(CN)_6]$.

For electrocatalytic activity studies, Phosphate buffer solution (PBS) pH=7 was used as supporting electrolyte. Solutions of Ascorbic acid (AA, 1mM), Catechol (CC, 1mM), Cysteine (Cys, 1mM) and Sulfide (SO_3^{2-} , 1 mM) were prepared daily by dissolving them in water.

RESULTS AND DISCUSSION

A typical multicycle CV voltammograms for electropolymerizations of $[H_2L]$, $[CoL]$ and $[NiL]$ on GFE were given in Fig.1. In the voltammograms of $[CoL]$ and $[NiL]$, the irreversible oxidation behavior was observed nearly 1.0 V at the first cycle. This oxidation peak was not observed in the voltammogram of the ligand. This situation was thought that the observed irreversible oxidation behavior due to the electrochemical activity of the

transition metal in the structure. Decrease of the peak current values after the first cycle, at the end of 25 cycles, supports the modification of the species to the electrode surface. Thus, the electrode surfaces has changed and gained a new character after modification of electrodes with metal complexes and the electrochemical behavior of the electroactive species has also changed [21]. The electrochemical stability voltammograms (successive CVs) were also given in Fig.1. Stability voltammograms have given to get the information about the stability and electroactivity of films obtained on GFE with investigating of electrochemical behavior during successive cycles. If the coating material is stable on modified surfaces, it is expected that in the voltammogram taken in the electrolytic solution will be no current change by repetitive potential scans in the anodic or cathodic direction. In particular, the fact that the current decline with sequential scans is that film degrades and is beginning to lose electrochemical stability (charge storage and unloading) [22]. When voltammograms are investigated, it is observed that there is a current change for modified surfaces after the first cycle. It is believed that this decrease in current is due to the removal of adsorbed monomers from the surface during cycling. No change in current is observed in subsequent cycles and the films on the electrode surfaces appear to maintain their stability during potential scanning.

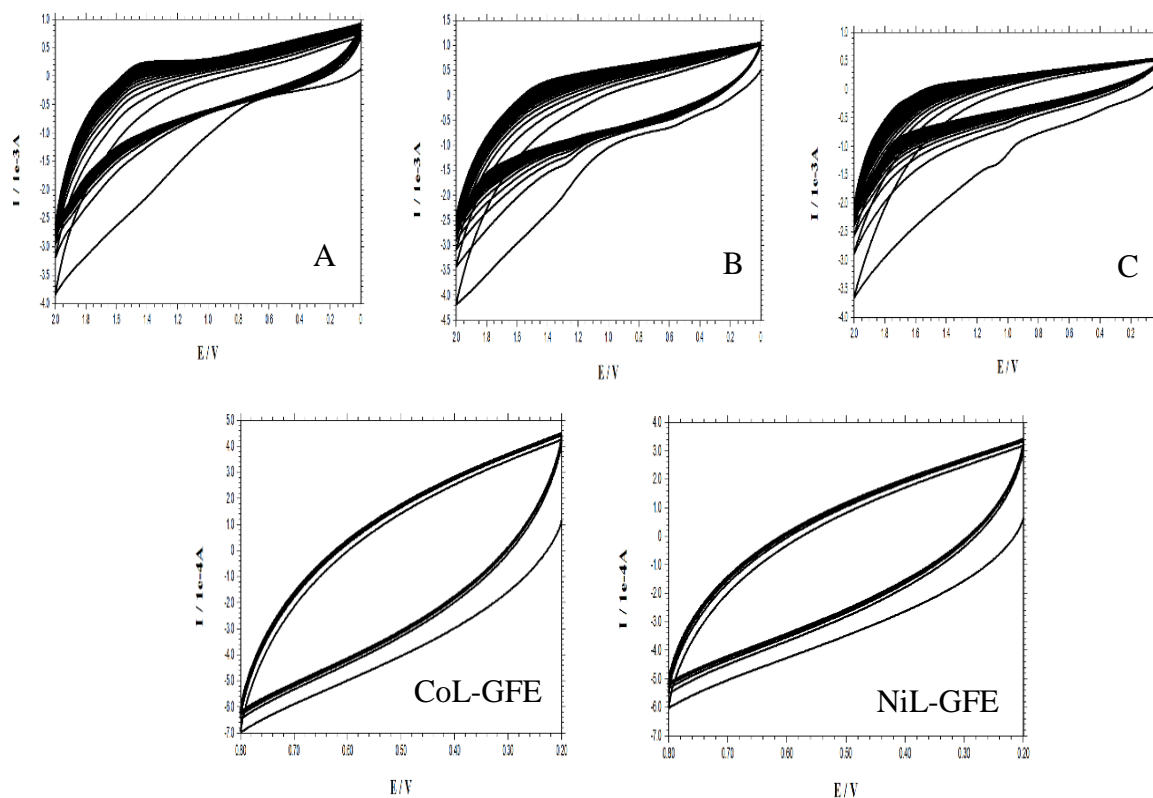


Fig.1. Multicycle voltammograms of [H₂L] (A); [CoL] (B) and [NiL] (C) in 0,15 M LiClO₄/acetonitrile solution as supporting electrolyte at GFE; Successive CVs of [CoL] and [NiL] films in 0.3 M KCl solution at 0.2-0.6 V potential range.

Electrochemical characterization of CoL-GFE and NiL-GFE surfaces were carried out using ferrocene and ferricyanide redox probes. Redox probes are usually reversible species with fast electron transfer at the surface of the bare electrode. Electrochemical behavior of redox probes on the modified electrode surface may differ from that of electron transfer kinetics. Such differences and similarities from time to time may provide information at the stage of modification during the electrochemical characterization [23, 24]. The cyclic voltammograms of the modified surfaces and the bare GFE with redox active molecules are shown in Fig.2. When voltammograms are evaluated, it appears that electron transfer of ferrocene is almost completely inhibited at the modified electrodes. For ferricyanide, electron transfer was observed to be blocked in large amounts on the surface of the modified electrodes compared to the bare GFE, but the electron transfer of the ferricyanide on the modified surface was found to be carried out at a certain amount by electroactive species diffusing from possible pinholes.

From the Nyquist plot given Fig. 2., it appears that the charge transfer rate of the [Fe(CN)₆]^{3-/4-} redox couple on the bare GFE surface is higher than the modified surfaces. It is understood that the lower value of the charge transfer resistance, which is effective in the high frequency regions on the

bare GFE surface, is observed at higher values, which is also effective in the lower frequency regions on the modified surfaces.

SEM images of [CoL] and [NiL] films were recorded in order to investigate the surface morphology and structure. The SEM images were given in Fig.3. It can be easily seen from SEM images that the crystalline structures occurred on the electrode surfaces after electropolymerization different from the bare GFE surface belongs to metal complexes.

In the UV spectrum of the [CoL] and [NiL] films, the band was observed at range of 330–450 nm were attributed to the *n*- π^* transition of the non-bonding electrons present on the nitrogen of the azomethine group of the Schiff base moiety [25]. In addition, the weak bands observed in the 500–700 nm region can be attributed to *d*-*d* transitions of the metal ions [26].

Cobalt and nickel ions distribution at modified surfaces were illustrated as red points at spectrum of SEM-EDX mapping analysis (Fig.3.). According to the SEM-EDX analysis, percentage distribution of cobalt and nickel ions on modified electrodes were determined as 0.50% and 0.54% respectively. These results have also give an important evidence about the electropolymerization of [CoL] and [NiL] onto GFE surfaces.

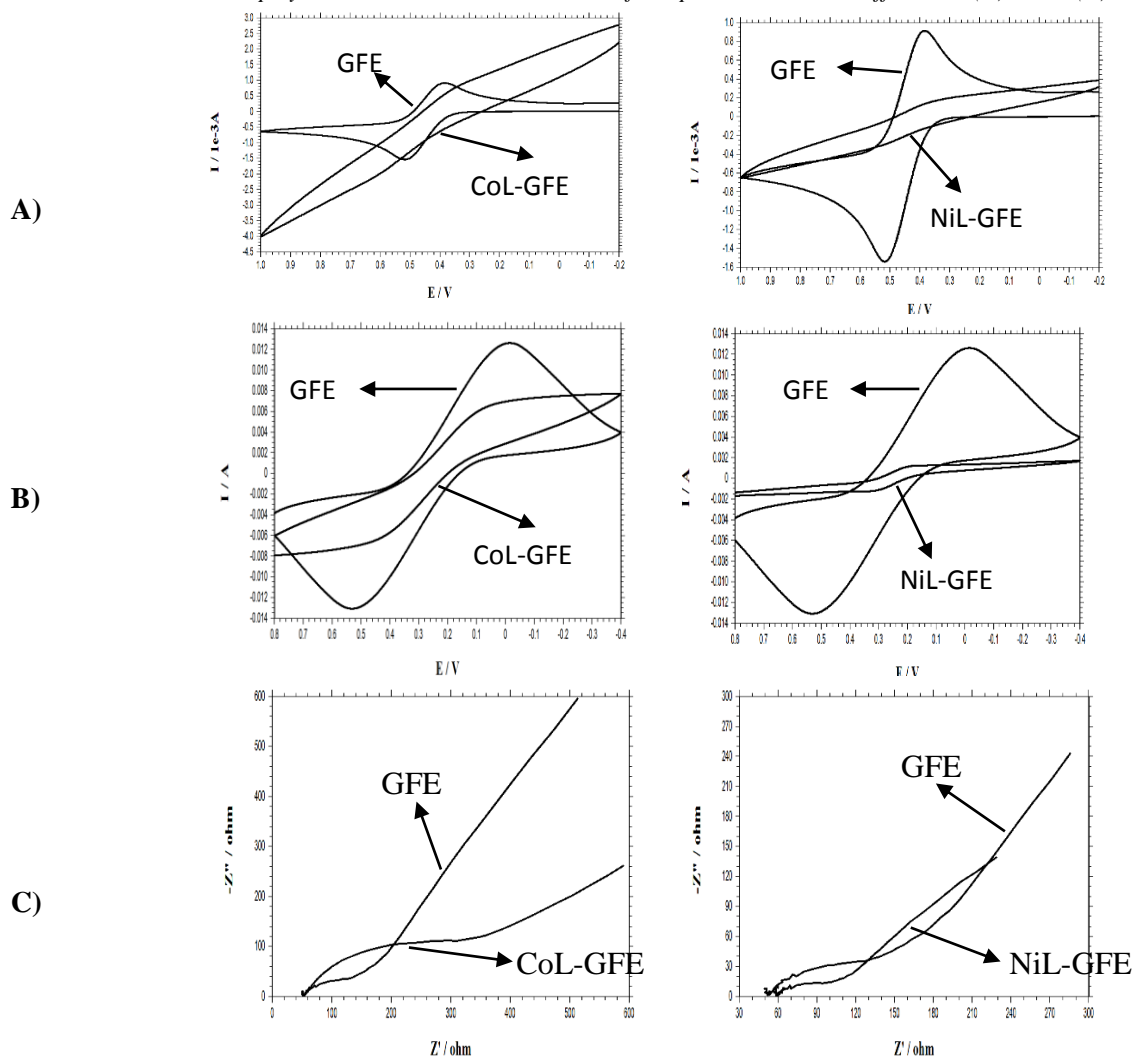


Fig. 2. Cyclic voltammograms of 1 mM (A) ferrocene (in acetonitrile containing 0.1 M LiClO₄), (B) ferricyanide (in 0.1 M KCl), scan rate is 100mVs⁻¹ and (C) Nyquist plots for bare GFE and modified GFEs in [Fe(CN)₆]^{3-/4-} (in 0.1 M KCl), frequency range is 100kHz-0.05 Hz.

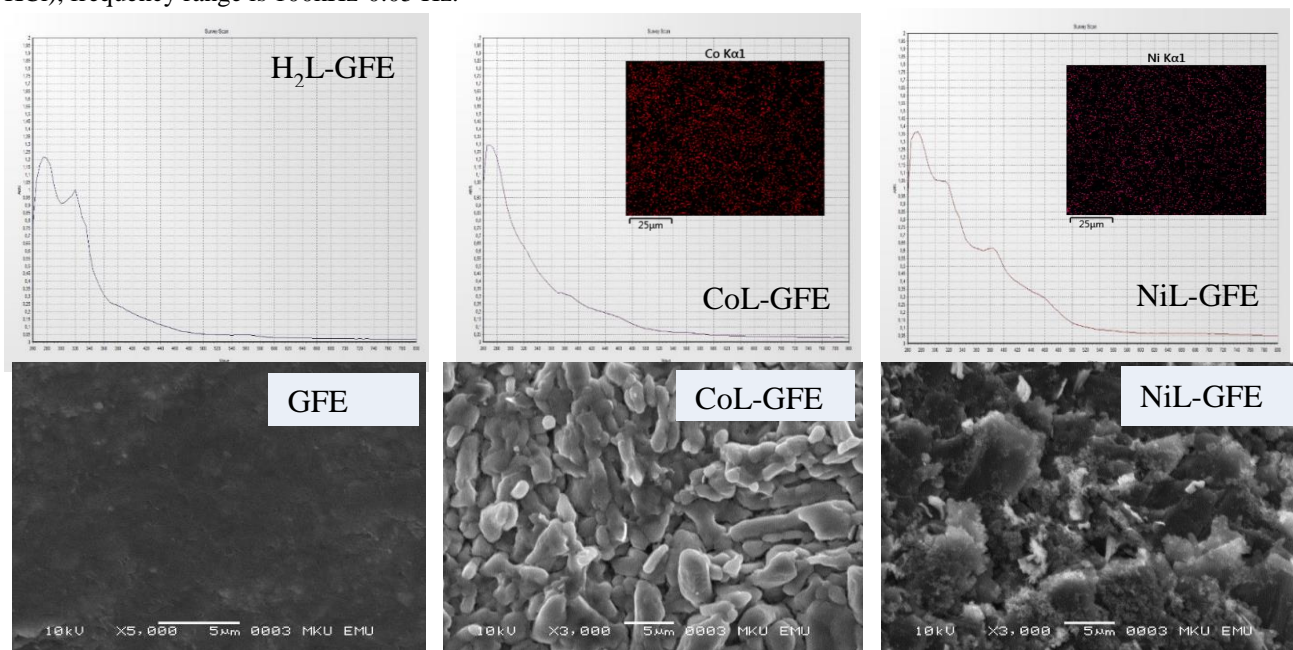


Fig.3. UV-Vis spectrums for H₂L-GFE, CoL-GFE and NiL-GFE; SEM-EDAX mapping analysis for CoL-GFE and NiL-GFE and SEM micrographs for bare GFE, CoL-GFE and NiL-GFE.

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FT-IR spectra of NiL monomer, H₂L-GFE and NiL-GFE film are shown in Fig.4. In the spectra of NiL-GFE film, the bands are broader than the bands belongs to monomer. It is clear that after electropolymerization, due to either increasing molecular weight or the molecular weight distribution of the polymers, the signals of polymers become broader than their monomers [27, 28]. This result is significant evident for polymer formation in this study. At the same time, the presence of different vibration bands from the ligand known to belong to the metal complex at low wavelength values supports the presence of metal on the modified surfaces in accordance with other analysis methods [29].

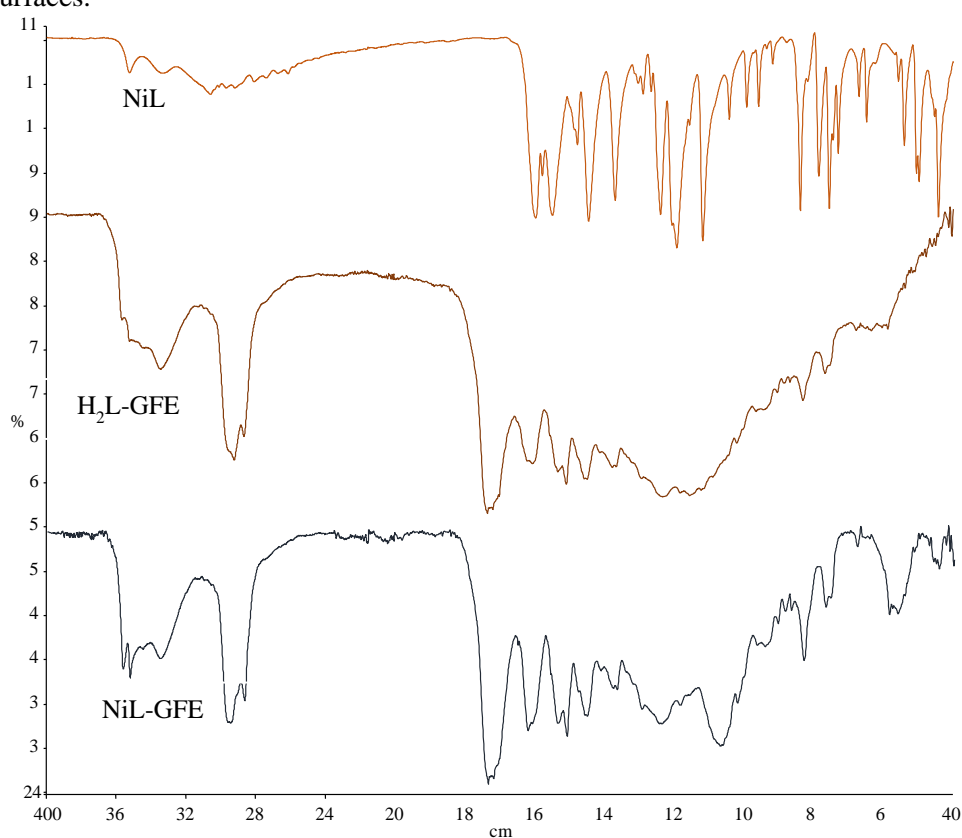


Fig.4. FT-IR spectra of [NiL] monomer, H₂L-GFE and NiL-GFE.

Catalytic activity studies for DA, AA CC and Cys were investigated at CoL-GFE and for CC and Cys were examined at NiL-GFE in pH=7 phosphate buffer solution and were presented in Fig.5-6. As a result of these studies, although NiL-GFE and CoL-GFE modified electrodes have almost the same catalytic activity potential, it has been found that CoL-GFE possesses comparatively better catalytic effect.

As can be seen in the voltammograms (Fig.5., Fig.6.), best electrocatalytic activity was obtained at CoL-GFE for CC oxidation in pH=7 PBS. In

comparison with the bare GFE, at this modified electrode, anodic peak current belongs to CC oxidation has increased for six times peak potential of CC oxidation appeared more positive potential value at modified electrode than bare GFE and peak shape was more sharply at modified electrode than bare electrode. Similar results were obtained for NiL-GFE in terms of the catalytic activity on CC oxidation. Additionally less significant catalytic activity was observed upon AA, Cys and sulfite bioanalytical species at CoL-GFE and for Cys at NiL-GFE, too.

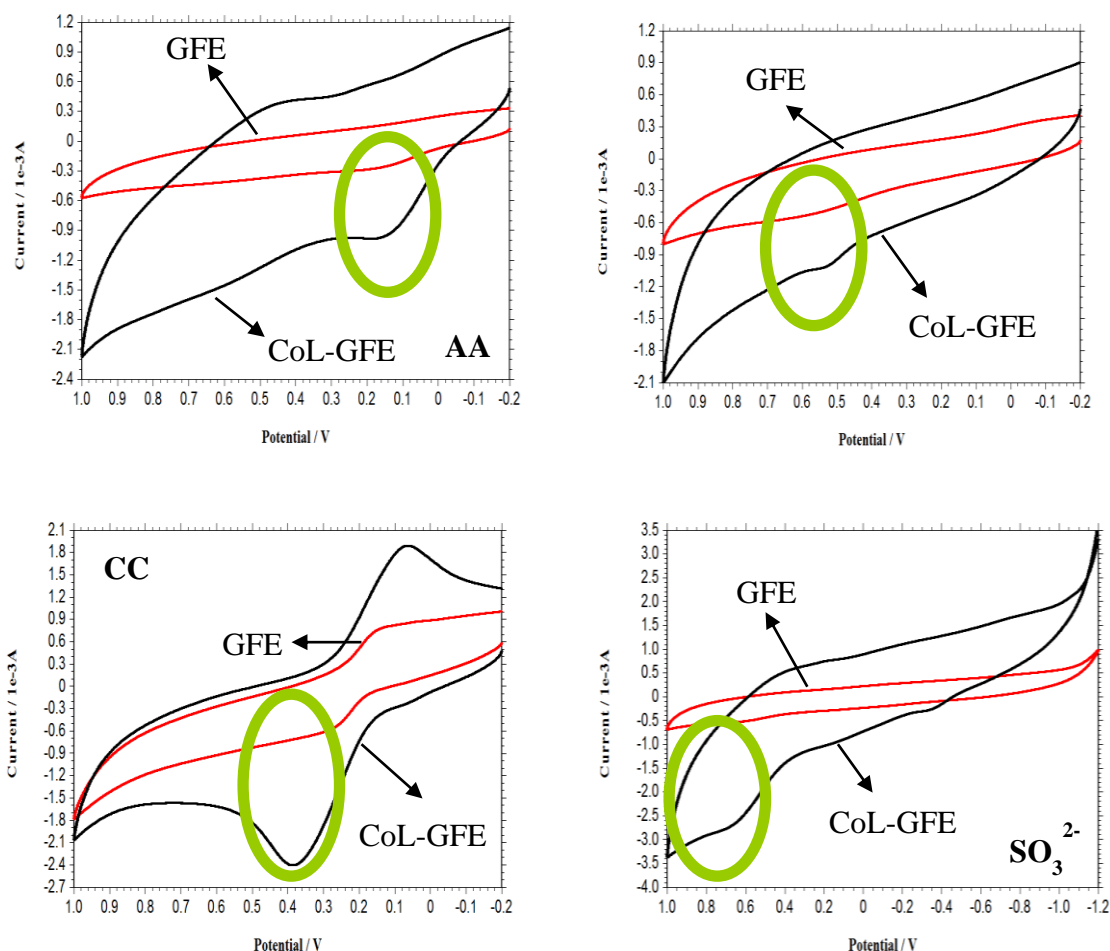


Fig.5. CVs of AA, Cys, CC and SO_3^{2-} at bare GFE and CoL-GFE in pH=7 PBS scan rate is 100 mVs^{-1} .

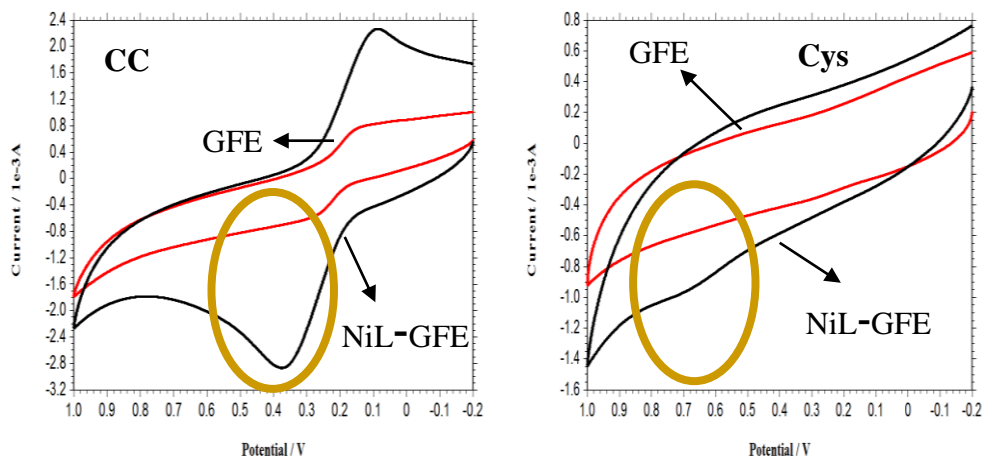


Fig.6. CVs of CC and Cys at bare GFE and NiL-GFE in pH=7 PBS, scan rate is 100 mVs^{-1} .

CONCLUSIONS

This study shows that metal complexes have been successfully coated onto the Ggraphite electrode surfaces by using electrochemical methods. In this way, alternative electrode materials can be developed for many various applications. Modified surfaces were characterized by electrochemical, spectroscopic and microscopic techniques. The results of the characterization studies have shown

that the films are homogeneous, very stable and conductive. Modified electrodes have potential use for bioanalytical species at electroanalytical applications.

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