

Electro-Oxidation of Iso-Propanol on Poly-Ni(II)-Unsymmetrical Tetradentate Schiff Base Complex Modified Vitreous Carbon Electrode

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Abstract:

Nickel Schiff bases complexes in alkaline aqueous solution offer efficient electrode molecular materials for the electrocatalytic activation of alcohols

The electrochemical oxidation of iso-propanol using poly-nickel unsymmetrical tetradentate schiff base complex (poly[Ni(II)-L.pyridine]⁺2Cl⁻) modified vitreous carbon electrode is described.

Unsymmetrical tetradentate Schiff base complex of nickel (II) can be electropolymerized onto vitreous carbon surface in alkaline solution to give electroactive films strongly adhered on the electrode surface. In alkaline solution, these poly[Ni(II)-L.pyridine]⁺2Cl⁻/GC films present the typical voltammetric response of a surface-immobilized redox couple, as can be anticipated for the Ni²⁺/Ni³⁺ transitions into the film.

In addition, the films exhibit a potent and persistent electrocatalytic activity towards the oxidation of iso-propanol.

Keywords: Poly-nickel unsymmetrical tetradentate Schiff base complex, Iso-propanol, Electro-oxidation.

I-Introduction

Several studies are reported in the literature on the use of Schiff base complexes bearing electropolymerizable groups, in alkaline media these are capable to form polymeric films at electrode surface, and the resulting modified glassy carbon electrodes have shown interesting catalytic properties towards the electro-oxidation of alcohols[1, 2, 3, 4]. Nickel macro complexes (cyclam, salen, porphyrins, phthalocyanines etc.) in alkaline aqueous solution offer efficient electrode molecular materials for the electrocatalytic activation of alcohols[5, 6]. Although the electrocatalytic properties of nickel Schiff bases, and typical behaviour when “electropolymerized” films in aqueous alkaline solution have been well studied[7, 8, 9, 10]. During the last decade, it has been shown that nickel Schiff bases complexes especially salen = ethylenebis(salicylideneaminato) can be easily deposited onto an electrode surface in alkaline solutions to form stable modified electrodes that catalyse the oxidation of several alcohols, [8,11, 12]. Few data exist on the electrochemical behavior and electrocatalytic activation of alcohols of dissymmetric metal Schiff base salen

complexes [13]. The oxidation mechanisms of methanol [14,15], ethanol [16,17,18] and iso-propanol [15,19] have been widely studied in alkaline media with cyclic voltammetry. Especially, direct 2-propanol fuel cells have attracted more and more attention as 2-propanol is the smallest secondary alcohol, less toxic than methanol and its electrochemical oxidation is of great interest due to its particular molecular structure [20]. The direct alcohol fuel cells using 2-propanol as fuel show much higher performance than direct methanol fuel cells and a much lower crossover current [21-23]. The purpose of the present work is the detailed investigation of iso-propanol oxidation on poly-nickel unsymmetrical tetradentate schiff base complex (poly[Ni(II)-L.pyridine]⁺2Cl⁻) modified vitreous carbon electrode.

II-Experimental

All chemicals used in this work were analytical grade of Aldrich chemical origin and were used without further purification. All solutions were prepared by doubly distilled water. The monomer [Ni(II)-L.pyridine]⁺2Cl⁻ complex was synthesized according to published procedures by template condensation of dehydroacetic acid, pyridine and ethylenediamine with Ni Cl₂.4H₂O dissolved as well in methanol [24]. Electrochemical measurements were carried out in a conventional three-electrode cell powered by an electrochemical system comprising an VOLTALAB system with PGSTAT 300 PZ. For electropolymerization experiments, the poly- [Ni(II)-L.pyridine]⁺2Cl⁻ films were grown from a solution of 1 mM [Ni(II)-L.pyridine]⁺2Cl⁻ monomer in water, containing 0.1 M sodium chloride (NaCl) using cyclic voltammetry and cycling the potentials between 0 and 0.8V. A saturated calomel electrode (SCE) wire was reference electrode, the working electrode was vitreous carbon (VC, area = 0.03 cm²) and the counter electrode was a platinum wire. The vitreous carbon surface was polished with sand paper and 0.05 μm alumina to a mirror finish and was subsequently rinsed with distilled water. All experiments were performed under an atmosphere of argon gas and were performed at ambient temperature 22 ± 3 °C.

Experiments were performed in order to study the oxidation effect of iso-propanol on the unmodified and modified vitreous carbon electrode. For these experiments, 50 cyclic voltammograms were recorded in 1 mM [Ni(II)-L.pyridine]⁺2Cl⁻ monomer in aqueous 0.1M NaOH solution and the potential was cycled between 0.0 and +0.8V/SCE (at 25 mV/s).

III-Results and discussion

III-1.Electropolymerization of [Ni(II)-L.pyridine]⁺2Cl⁻ onto VC electrode

Modification of VC electrode was carried out by electropolymerization of [Ni(II)-L.pyridine]⁺2Cl⁻ in solution by multiple scan cyclic voltammetry. The potential was cycled from 0.0 to +0.8V at 25 mV/s while the VC electrode was immersed in a 0.1Mm solution of [Ni(II)-L.pyridine]⁺2Cl⁻ in aqueous 0.1M NaOH. Fig. 1 A shows the electroactive film growth pattern obtained under continuous potential cycling. During the first scan electrochemical response ascribed to the oxidation of the Ni²⁺ to Ni³⁺.

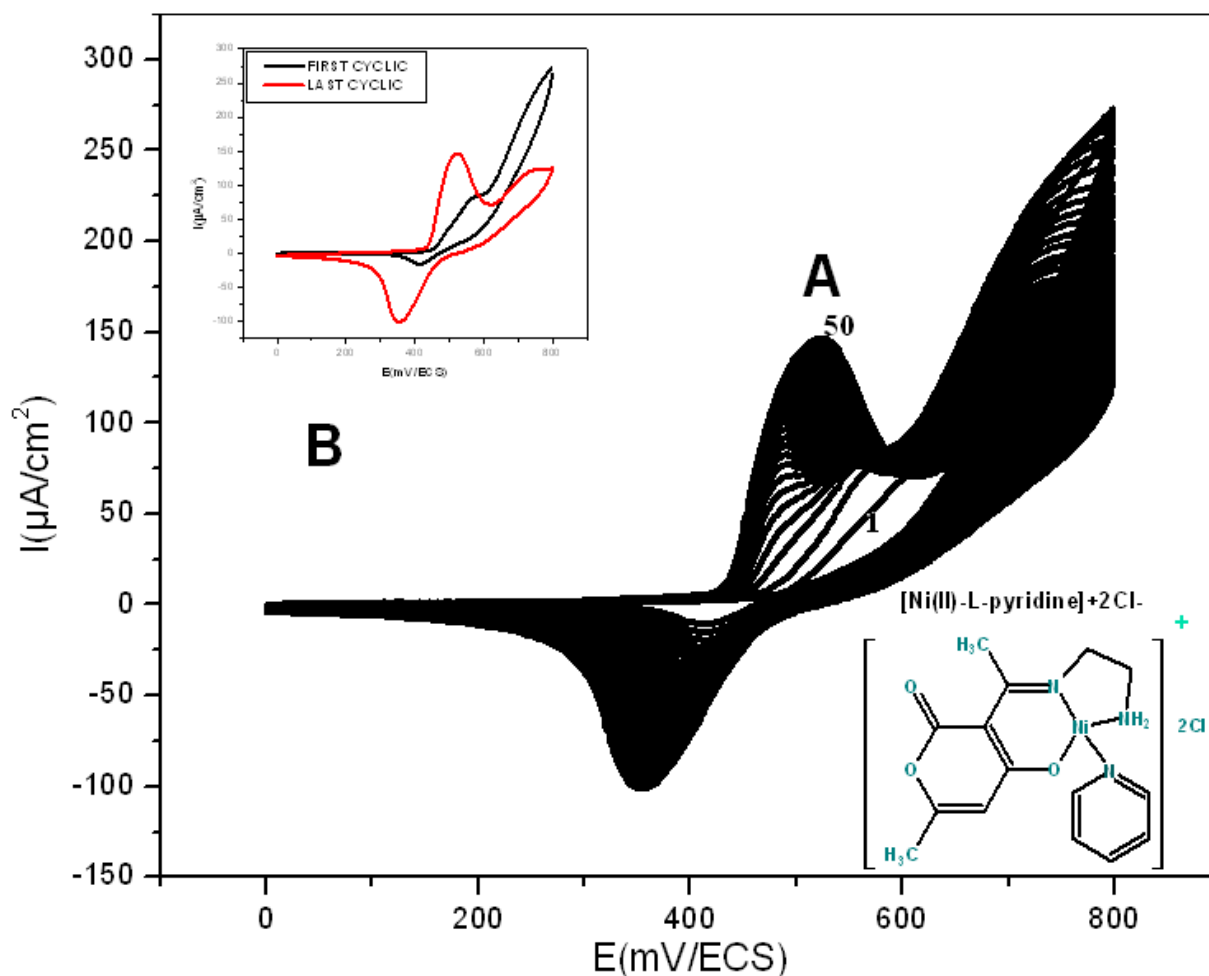


Fig.1. Cyclic voltammograms (A) of 0.1mM of $[\text{Ni(II)-L-pyridine}]^+2\text{Cl}^-$ (structure inset) complex at VC electrode in 0.1M NaOH (pH=11) during modification of the electrode surface. The inset (B) shows the first and last cyclic of $\text{poly}[\text{Ni(II)-L-pyridine}]^+2\text{Cl}^-$.

The anodic and cathodic peaks observed are due to the redox reaction of the $\text{Ni}^{2+}/\text{Ni}^{3+}$ couple in the $[\text{L-pyridine}]^+2\text{Cl}^-$ polymeric film. Oxidation of Ni^{2+} to Ni^{3+} in the film takes place at a potential of +0.490V and the corresponding reduction is observed around +0.353V.

The potential was continuously cycled between 0 and 0.8V at 25 mV s⁻¹ on the vitreous carbon electrode was immersed in monomer solution of 1 mM $[\text{Ni(II)-L-pyridine}]^+2\text{Cl}^-$ in aqueous 0.1 M NaOH. It can be seen that an ill-defined redox couple appears during the first scan which increases and becomes well defined when the potential scans are repeated. The continuous increase in the amplitude of the voltammometric peaks, around 0.40V, indicates that the film has been formed as a result of the anodic deposition of the Schiff base complex. The mechanism of electrooxidative deposition of the nickel complex is not fully clear at present. By the same manner, the electropolymerization of the copper complex of (half-unit = 2,6-diacetylpyridine-mono(ethylenediamine)) was performed, which led to an electroactive polymeric film whose electrocatalytic properties. [9]. One can cite the example of the electrooxidative polymerization of, a 3-[1-(2-amino-phenylimino)-ethyl]-6-methylpyran-2,4-dione Schiff base. [25, 26].

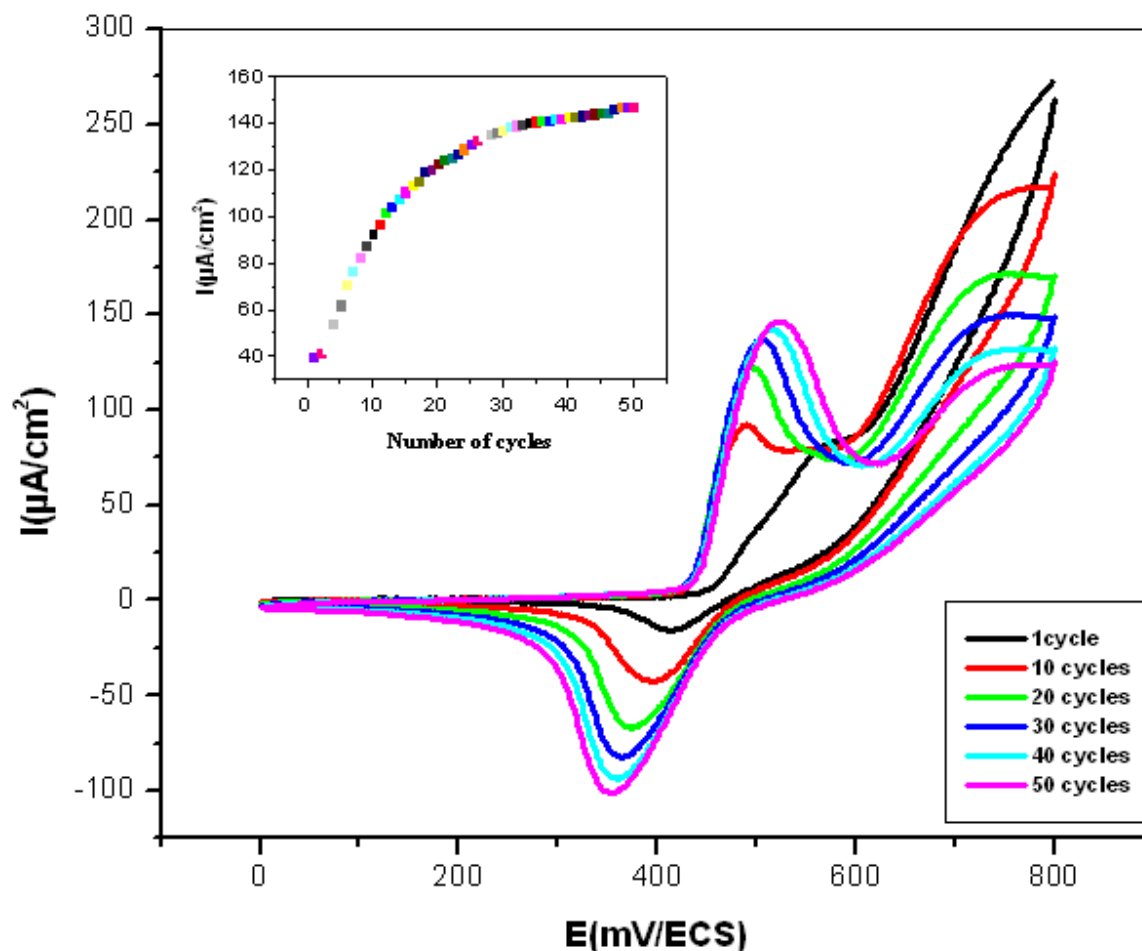


Fig.2. Dependence of anodic peak current I of the film of nickel compounds on the number of cycles.

Electropolymerizing scans (and then increases but not linearly), indicating that the electropolymerization process progresses during the cycling of the potential. At the initial stage (1–15 cycles), the “nickel” film grows very slowly, (This can be related to the difficulties in nucleation of a new phase formed by nickel compounds.

The polymeric film obtained shows a high adherence to the vitreous carbon surface. When a poly-[Ni(II)-L-pyridine]⁺2Cl⁻/VC electrode is transferred to a 0.1M NaOH solution, containing no monomer, the cyclic voltammograms obtained show the typical response of the Ni²⁺/Ni³⁺ redox couple (Fig. 3b). In order to check the electrochemical stability of the polymeric film, the potential was continuously cycled from 0.0 to +0.8V at 100 mV/s and the cyclic voltammogram was registered after each 5 cycles

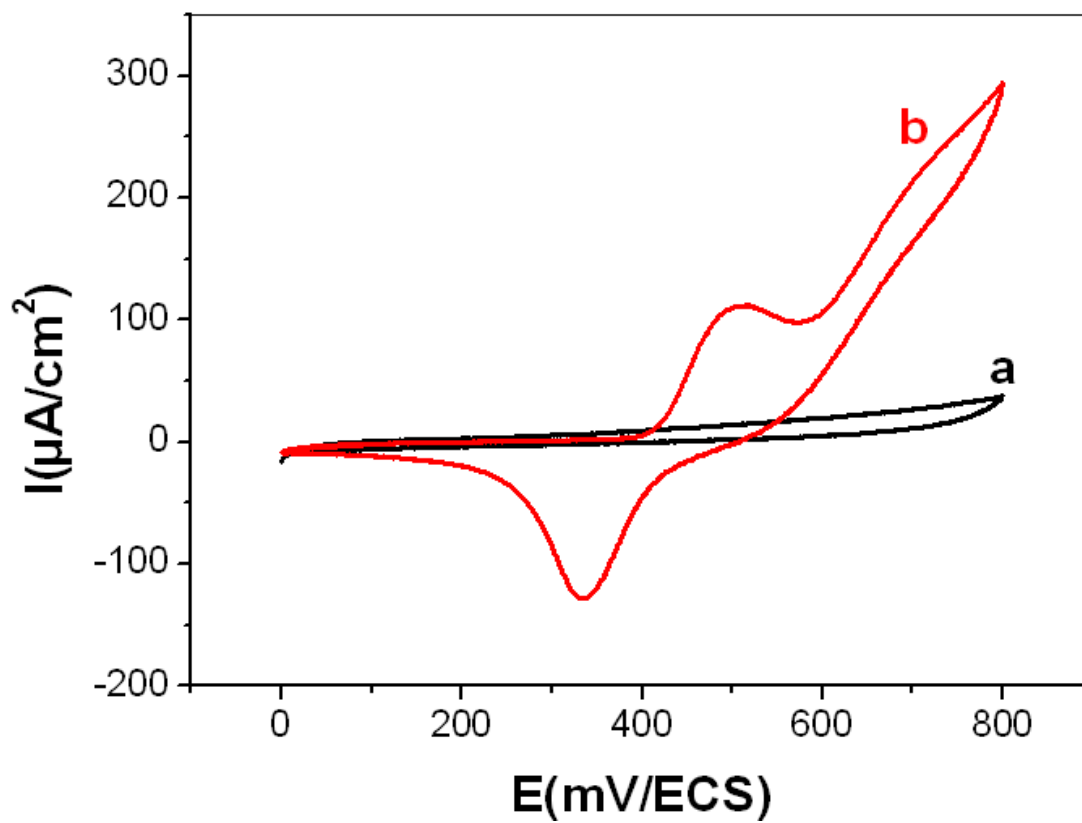


Fig.3. Cyclic voltammograms of (a) unmodified and (b) poly-[Ni(II)-L-pyridine]⁺2Cl⁻/VC modified electrode prepared by 50 electropolymerizing in 0.1 M NaOH solution(pH=11). Scan rate: 100 mV/s.

III-2.The Effect of Scan Rate

The effect of the scan rate on [Ni(II)-L-pyridine]⁺2Cl⁻ VC modified electrode peak current was investigated. As shown in Fig.4, the anodic peak current increased and the peak potential shifted positively with increasing of scan rate.

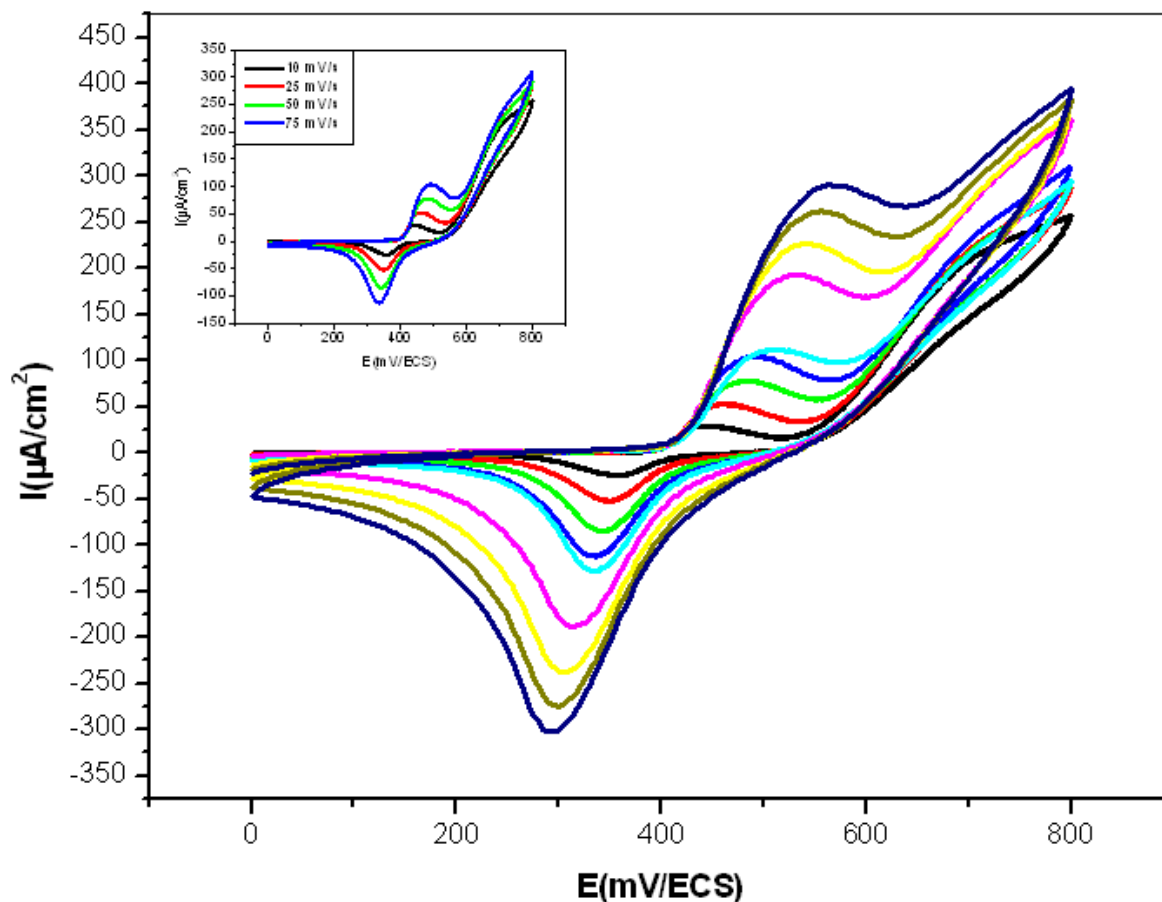


Fig.4. Cyclic voltammetric response of VC electrode modified with a film derived from $[\text{Ni(II)-L-pyridine}]^+2\text{Cl}^-$ in 0.1MNaOH (pH=11), at the following scan rates: 10mV/s; 25 mV/s; 50 mV/s; 75 mV/s; 100 mV/s; 200 mV/s; 300 mV/s; 400 mV/s; 500 mV/s.

Inset of figure 5 shows a plot of E_p versus $\log V$, The anodic peak shows a potential shift towards more positive values, while the cathodic peak is shifted towards more negative potential values as shown in Fig.4. For the surface confined electroactive species at small concentrations, the electron transfer coefficient, α and the charge transfer rate constant, k_s , can be estimated from their cyclic voltammetric response using the equations derived by Laviron[27].

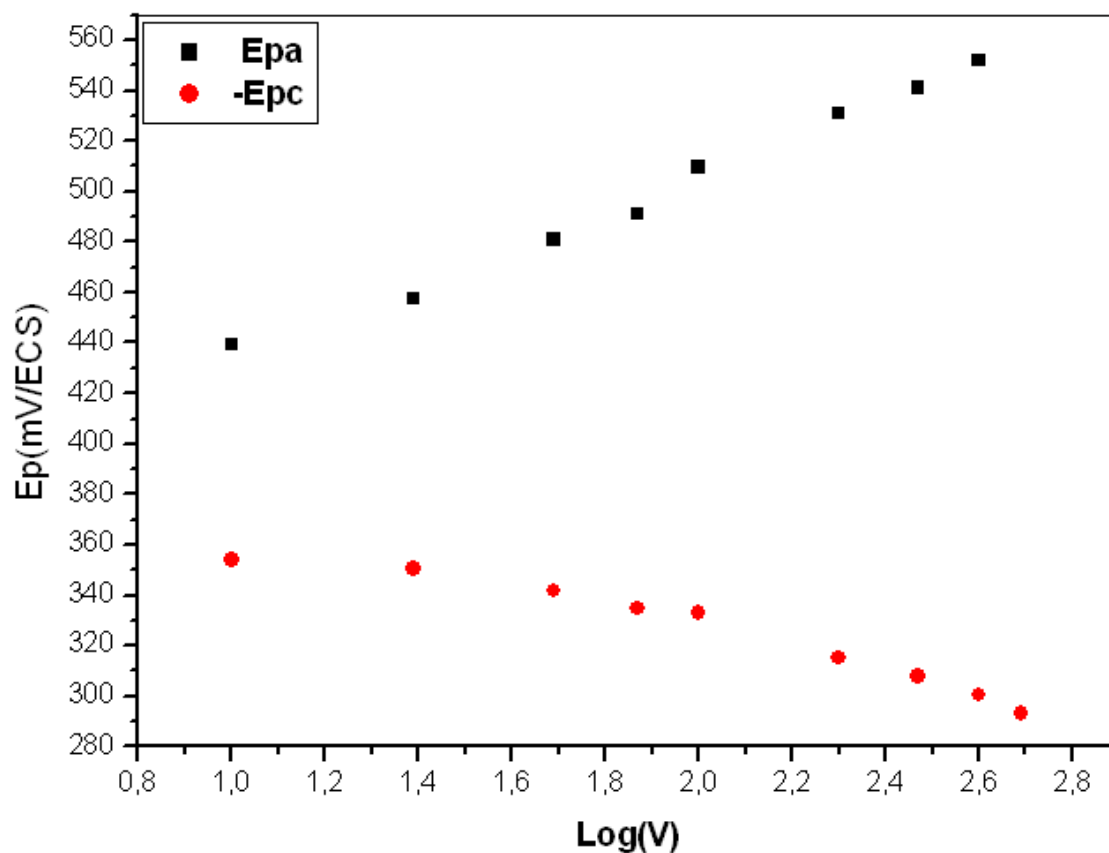


Fig.5: Laviron's plot showing the dependence of the peak potential on the logarithm of scan rate.

Inset of figure 6 shows a plot of I_{pc} versus $V^{1/2}$. The linearity suggests a diffusion process [28] of poly-[Ni(II)-L-pyridine]⁺2Cl⁻/VC modified electrode from the alkaline solution to the VC surface. This process could be related to counter-anion diffusion into and out of the modified electrode during the oxidation and reduction processes [29, 30]. Similar voltammograms have been obtained by the electrodes modified with high loadings of poly-[Ni(II)-L-pyridine]⁺2Cl⁻ film present a relatively slow redox transition between the substrate and the nickel redox centers[31].

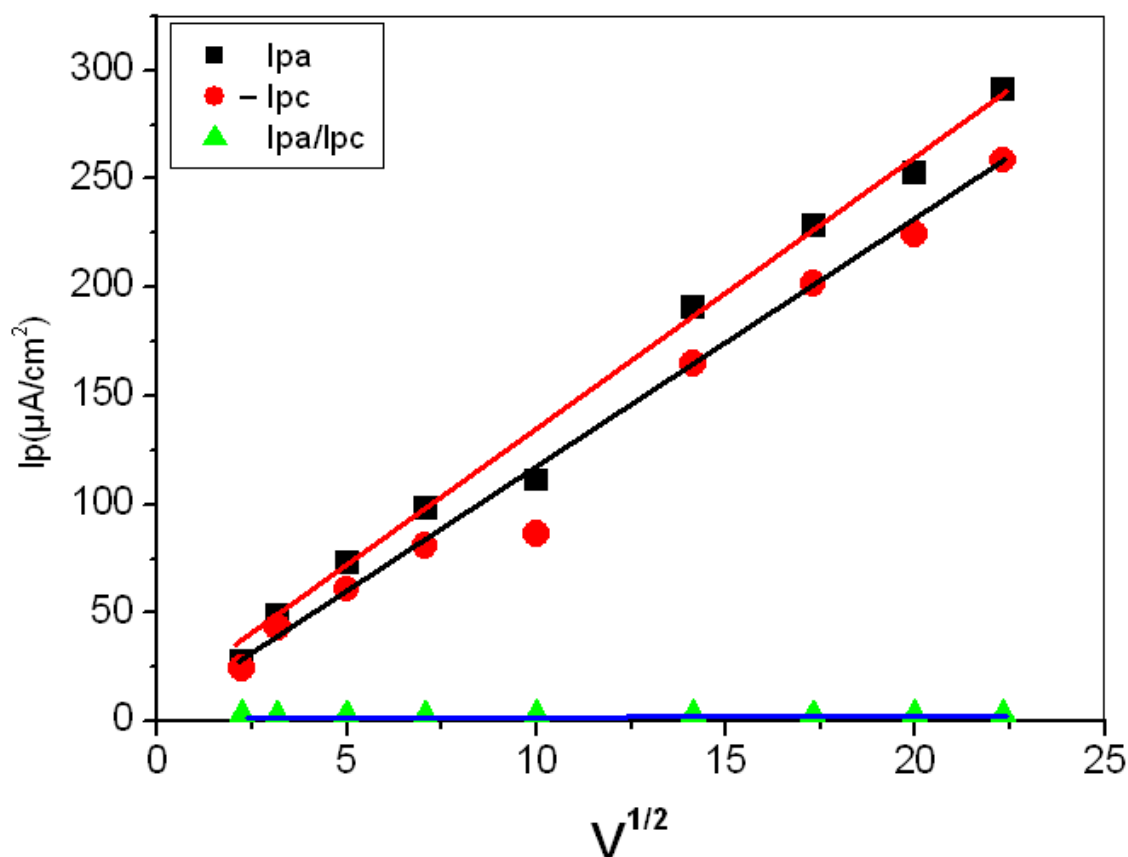


Fig.6: Plots of anodic and cathodic peak currents versus the square root of potential scan rate. Data was taken from the poly[Ni(II)-L-pyridine]⁺2Cl⁻ VC modified electrode in a 0.1M NaOH solution with potential scan rates of 10, 25, 50, 75, 100, 200, 300, 400 and 500 mV/ s.

III-3. Electrocatalytic Oxidation of Propanol-2 at Poly-[Ni(II)-L-pyridine]⁺2Cl⁻/VC Electrode

Poly-[Ni(II)-L-pyridine]⁺2Cl⁻ electrocatalytic activity on propanol-2 oxidation was investigated by cyclic voltammetry. Typical cyclic voltammograms of poly-[Ni(II)-L-pyridine]⁺2Cl⁻/VC in 0.1M NaOH solution without/ with 26mM propanol-2 / with 65mM propanol-2 at a scan rate of 100mVs⁻¹ are shown in curves a, b and c of Fig.7., respectively. An examination of the without propanol-2 curve a shows a ([Ni(II)-L-pyridine]⁺2Cl⁻)/([Ni(III)-L-pyridine]⁺2Cl⁻) redox transition [32,33]. The with propanol-2 curves b and c reveals the ([Ni(II)-L-pyridine]⁺2Cl⁻)/([Ni(III)-L-pyridine]⁺2Cl⁻) onset potential is slightly delayed. This may be due to higher ([Ni(II)-L-pyridine]⁺2Cl⁻) electron transfer resistance because of propanol-2 absorption on the NiIII active center. The curve b current in the 0.35–0.55V potential range is a catalytic oxidation process in which the NiIII species formed electrochemically on the electrode surface is reduced by the propanol-2 [32]. A similarly shaped cyclic voltammogram was observed by Matthew and Markiewicz[34], changwei Xu and Zhiquan [35], and Matthew and Markiewicz [36], and Jianping Lui and Jianping Ye [37], for propanol-2 oxidation in basic media on Pt, Pd, Pt/Ru electrodes modified.

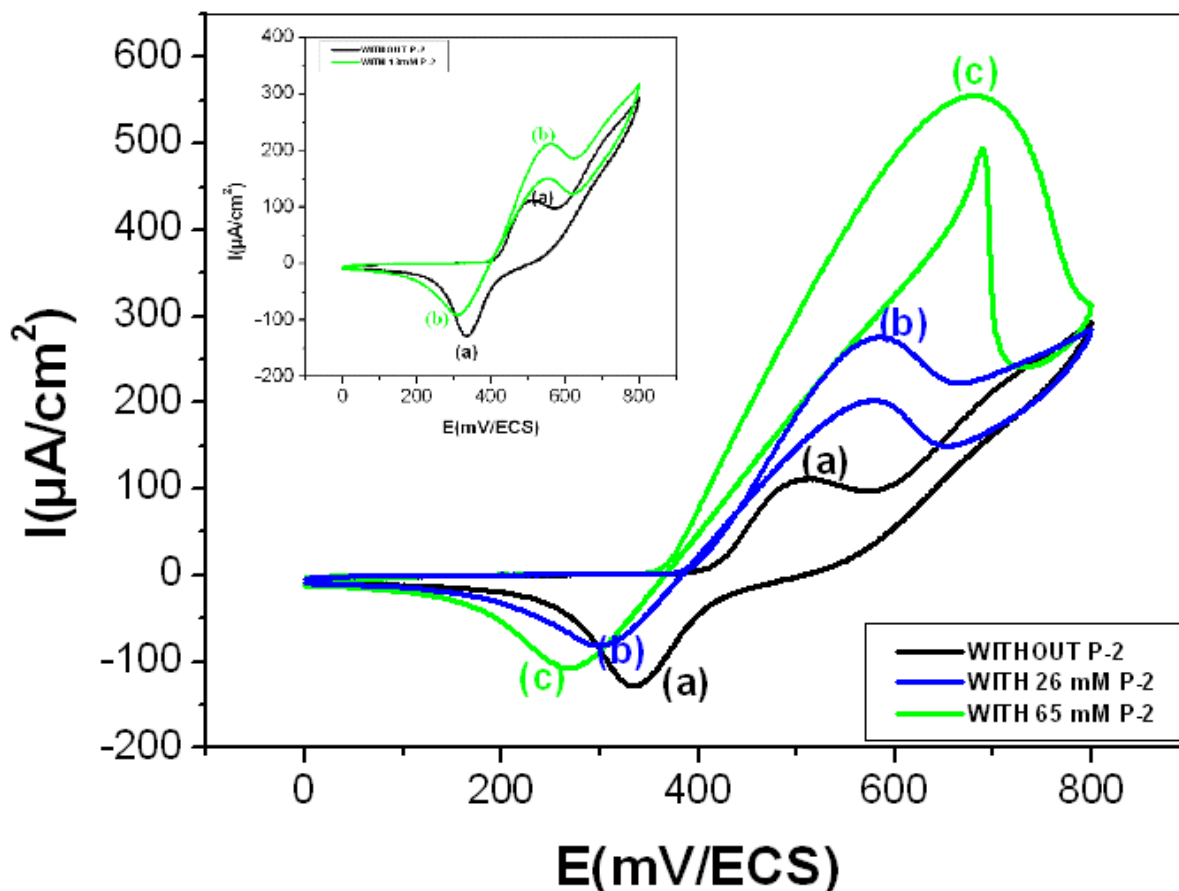


Fig.7. Cyclic voltammogram of the poly-[Ni(II)-L-pyridine]⁺2Cl⁻/VC electrode in 0.1M NaOH solution: (a) without 2-propanol; (b) with 26 mM 2-propanol; with 65 mM 2-propanol (c) .

Cyclic voltammograms of [Ni(II)-L-pyridine]⁺2Cl⁻ in 0.1M NaOH solution at a 100mVs⁻¹ scan rate for propanol-2 concentrations ranging from 0 to 26 mM are shown in Fig.6. Examination of the figure shows that propanol-2 oxidation onset potentials increase with increasing propanol-2 concentration. It was suggested above that onset delay follows from higher [Ni(II)-L-pyridine]⁺2Cl⁻ electron transfer resistance as isopropanol absorbs on the Ni(II) active center. By this model, higher propanol-2 concentrations result in greater numbers of Ni(II) active centers with absorbed propanol-2, with increasing onset delay following from increasing propanol-2 concentration.

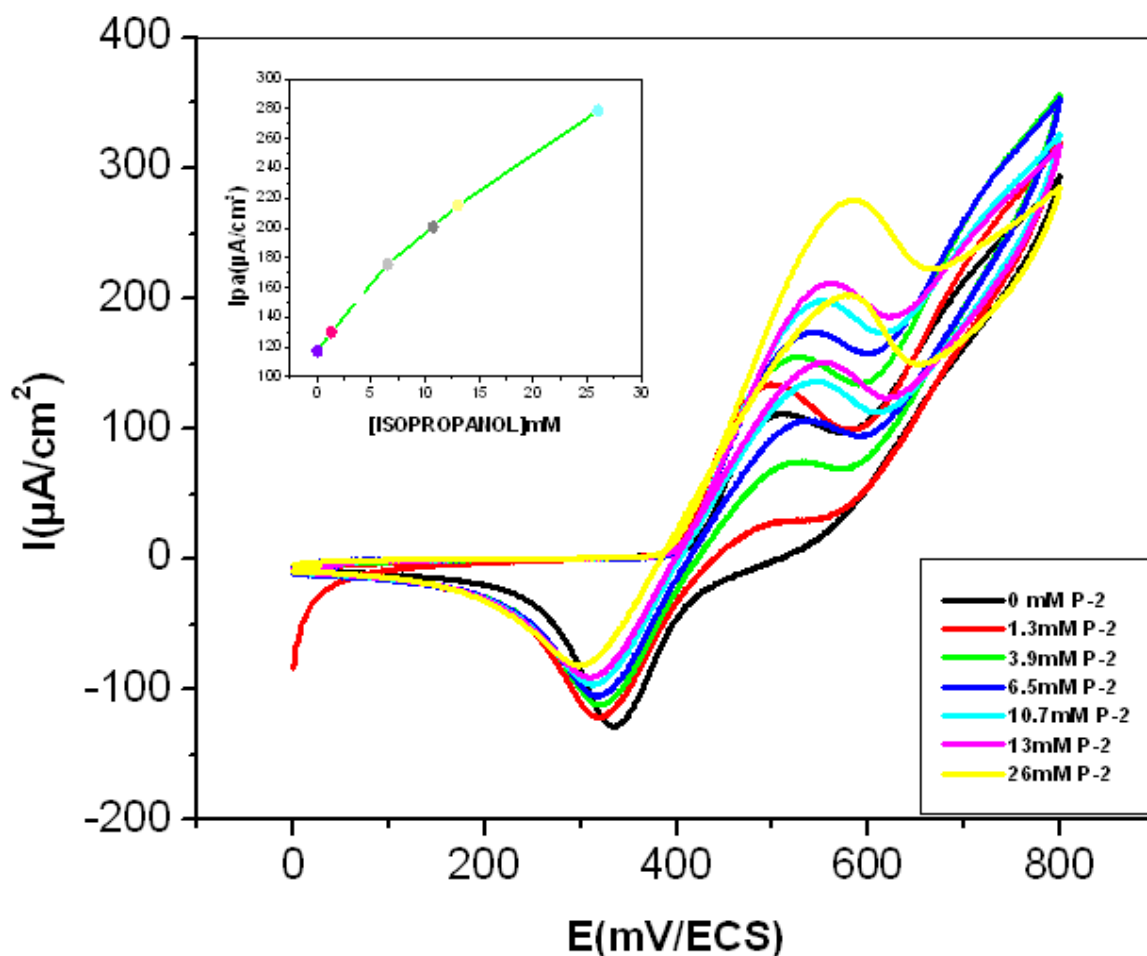


Fig.8.1. Voltammetric curves of propanol-2 oxidation on a poly-[Ni(II)-L-pyridine]⁺2Cl⁻/VC electrode at scan rate of 100mVs⁻¹ in 0.1M NaOH solution containing 2-propanol as follows: 0mM; 1.3 mM; 3.9 mM; 6.5 mM; 10.7 mM; 13 mM; 26 mM.

The effect propanol-2 concentration on the CV peak current and the peak potential of a [Ni(II)-L-pyridine]⁺2Cl⁻ modified vitreous carbon electrode was also investigated in a solution of 1.0 mol L⁻¹ NaOH. The results are shown in Fig. 9. It can be seen that in Fig. 9a the peak current for the catalytic oxidation propanol-2 increases with increasing concentration. Linear relationships between the CV peak current and the reactant concentration for propanol-2 can be observed in the concentration range of 0–0.5 mol L⁻¹. In Fig. 9b, it can be also observed that the peak potentials for both alcohols shift positively with increasing alcohol concentration. These results suggest that the catalytic oxidation of both alcohols is controlled by the diffusion of the reactant. The consistent increase in the oxidation peak currents of propanol-2 with reactant concentration, shown in Fig. 9 b, could be employed in the analysis of alcohol concentration.

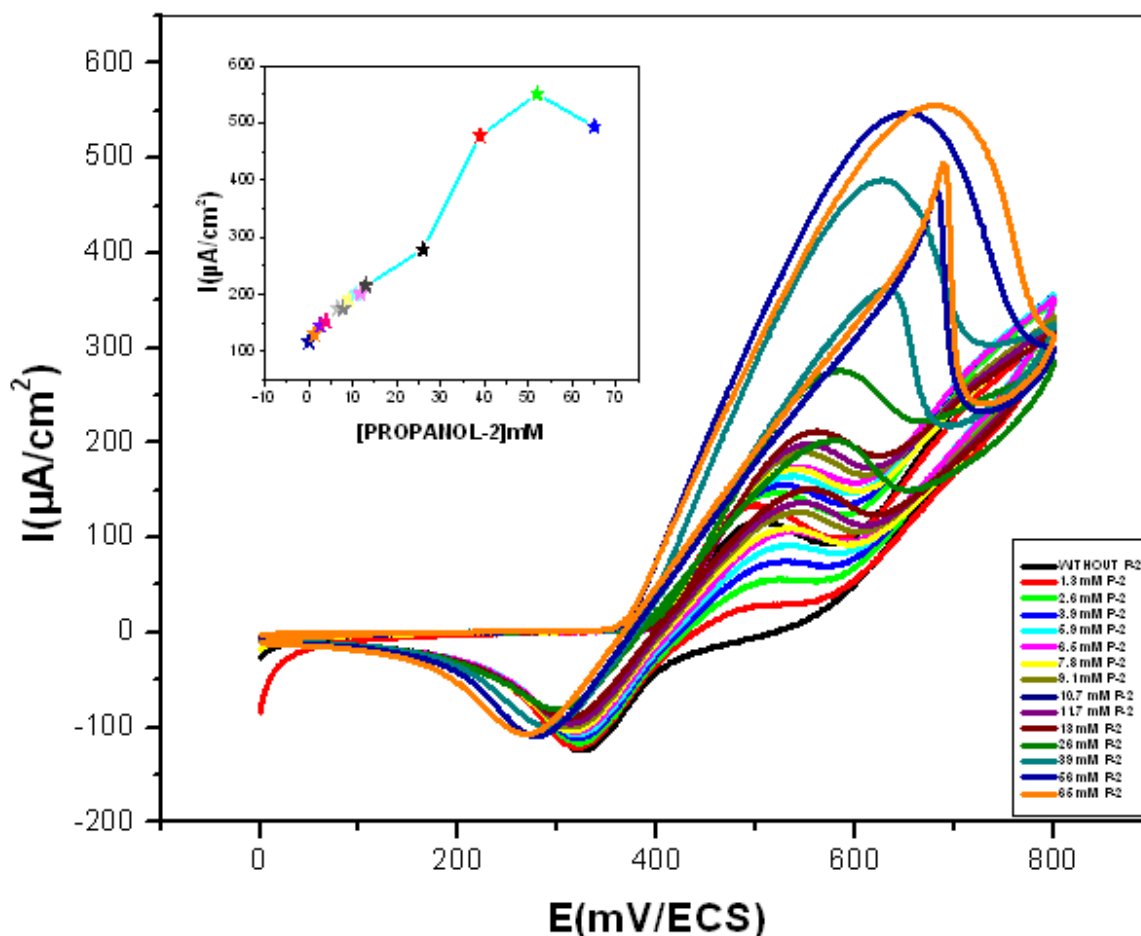


Fig.8.2. Voltammetric curves of methanol oxidation on a poly-[Ni(II)-L-pyridine]⁺2Cl⁻/VC electrode at scan rate of 100mVs⁻¹ in 0.1M NaOH solution containing 2-propanol as follows: 0mM; 1.3 mM; 2.6 Mm; 3.9 mM; 5.9 mM ;6.5 mM; 1.3 Mm; 10.7 mM; 13 mM; 26 mM.

They were propose that the mechanism up to the current maximum at low potentiels involves the electroxydation of propanol-2 to acetone, taking into consideration the reported observations made in acid [38-43] and in base [44,45,46,47] electrolytes.

IV-Conclusion

The preliminary in the present study show that Ni(II)-Unsymmetrical Tetradentate Schiff Base Complex [Ni(II)-L-pyridine]⁺2Cl⁻ can be electropolymerized onto vitreous carbon surface in 0.1M NaOH solution to give conductive polymeric films which present a high adherence to the electrode surface and good stability. After the polymerization and further conditioning steps the modified electrodes only present a redox activity that can be ascribed to the ([Ni(II)-L-pyridine]⁺2Cl⁻)/([Ni(III)-L-pyridine]⁺2Cl⁻) redox couple present in the film. In alkaline medium, the [Ni(II)-L-pyridine]⁺2Cl⁻ formed present a potent and persistent electrocatalytic activity towards propanol-2 oxidation. At low propanol-2 concentrations the rate of the catalytic process is controlled by diffusion while at high alcohol concentrations, the

reaction is governed by the kinetic of the interaction between propanol-2 and the oxidized nickel catalytic centers present in the film. The catalytic peak current shows a linear dependence on the concentration of propanol-2 in the solution up to 13 mM. In addition, the poly-([Ni(II)-L-pyridine]⁺2Cl⁻/VC electrodes can be used as effective catalyst for electro-oxidation of other short chain aliphatic alcohols, such as: methanol, ethanol, 1- propanol, and *n*-butanol.

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