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Electropolymerization using binuclear nickel (II) *Schiff* base complexes bearing N_4O_4 donors as supramolecular building blocks

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The supramolecular building blocks from nickel(II) bisalphen-type complex was reported. The conjugations through the bridge provide a flexibility of monomer in the electropolymerization stage. Thus, different structures can be obtained with the variation of electrochemical parameters used in the electropolymerization. The structural characterization and the electrochemical behavior in aqueous solution was also evaluated, which demonstrating that the electropolymerization mechanism was similar to observed to the classical salen polymers, but the molecular organization onto conductor substrate is different. The supramolecular structure of polymeric film allows observe the Ni^{I}/Ni^{II} and Ni^{II}/Ni^{III} redox couple by differential pulse voltammetry. Thus, the comproportionation constant and Gibbs energy were calculated by Ni^{I}/Ni^{II} redox couple. These characteristics make these polymer versatile materials the field of supramolecular chemistry and material science, in particular to application as sensor, in electrocatalysts and energy storage.

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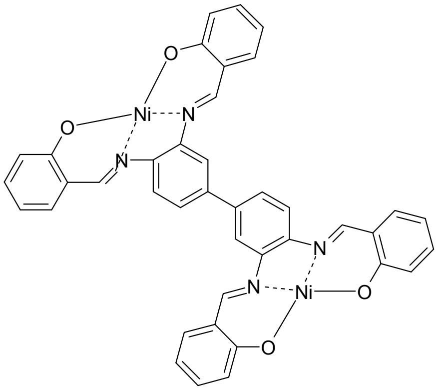
INTRODUCTION

The *salen* ligands play an important role in the development of sensor not only due to variety of transition metals that can be incorporated, but also the variety of ligand derivative from classics *salen*[1-3]. In addition, the *salen*-polymers containing transition metal complexes showed special interest, given their ease of preparation by electropolymerization as well as their conducting character in aqueous solution[4-9]. Among the principal metal-*salen* complexes, the binuclear complexes are currently of great interest in the field of supramolecular chemistry and material science[10-12] and have shown in some cases an unusual behavior, ascribed to conformational mobility. Thus, the development of new polymer with binuclear complex is raise the interest to application as electrochemical[13,14], chemiluminescent[15,16] and optical[17] sensors. The properties of metal complex derivate from bis(*salen*) can be similar to classical *salen* complex, since the bis(*salen*) complexes should have two independents moieties of *salen* ligand[18]. In particular, the 3,3'-diaminobenzidine framework offers versatile molecular building blocks. Supramolecular building blocks can be obtained from derivate of bis(*salen*) complexes in solution[19, 20]. Curreli *et al.*[19] described the synthesis of various bis(*salen*) complex and showed the supramolecular assemblies formation by combining two of these complexes with a ditopic ligand. On the other hand, the complexes derivate from bis(*salen*) can be applied to thin film formation. Byrd *et al.*[21] report the obtaining of polymeric films using a layer-by-layer method, where they showed that robust homogeneous films occurs due to strong coordination between the metal and the ligands.

However, the polymeric film obtained from nickel-*bisalphen* [Ni_2(*bisalphen*)] by electropolymerization was firstly reported by Aubert *et al.*[18]. In their study the polymer was formed by potential applied in saturated solution of Ni_2(*bisalphen*) in acetonitrile, due to low solubility. The authors evaluated that charge necessary for formation of polymer, where concluded that the polymeric formation be related with amount metallic cation present in the monomeric structure and the potential to over oxidize the polymer[18]. Thus, the present paper describes a complementary and comparative study of the electropolymerization stage, behavior electrochemical and morphological features were realized for the [Ni_2(*bisalphen*)] complex (Scheme 1) in tetrahydrofuran. Also, the comproportionation constant and Gibbs energy were calculated.



Scheme 1. Molecular structure of the *N,N',N'',N'''*-tetra*bis*(salicylidene)-3,3',4,4'-biphenylenetetraimino of *bis*-nickel(II).

EXPERIMENTAL

Apparatus

All voltammetric measurements were carried out in a 25 mL thermostatic glass cell containing three-electrodes: platinum electrode coated with a thin film of nickel-*bisalphen* polymer as working electrode (surface area of 0.071 cm^2), a saturated calomel (SCE) as the reference, and a platinum auxiliary electrode. The electrochemical measurements were conducted with a µ-Autolab type III (Eco Chimie) connected to a microcomputer and controlled by GPES 4.9 software. The Raman spectrums were obtained using a Renishaw Raman spectrometer with laser at an excitation wavelehgth of 663 nm. The image of optic microscopy was obtained by Leica optic microscopy, DMRX model (Eyepiece lens of 10x and objective lenses of 50x) for the polymer formed onto platinum surface. The image of scannig electron miscroscopy (SEM) using a Carls Zeiss microscopy model EVO LS15 and the atomic force microscopy (AFM) using a Nanosurf microscope model Easyscan 2, tapping mode (intermittent contact) and a resolution of 512 dots/line, were obtained to polymer formed onto ITO glass.

Synthesis of [Ni_2(b*isalphen*)]

The synthesis of *bisalphen* (*N,N',N'',N'''*-tetra*bis*-(salicylidene)-3,3',4,4'-biphenylenetetraimino) ligand was prepared as previously described in the literature[18]. The *bisalphen* ligand (1.58 mmol) was dissolved in ethanol (50 mL) and slowly added dropwise over a suspension of nickel(II) acetate (3.16 mmol) in the same solvent (50 mL). The solution was refluxed for 36 hours (at 60 ºC), and the red precipitate was filtered and recrystallized from methanol. The obtained product was stored in vacuum at room temperature. FTIR (ν cm^{-1}) 2651 $-OH_{ph}$, 1608 C=C, 1527 C=N, 1362 $>C-O_{ph}$, 1023 breathing ring, 765 Ni–O. UV-*vis* (nm) 262 ($\pi\rightarrow\pi^*$), 312 ($\pi\rightarrow\pi^*$), 388 ($n\rightarrow\pi^*$), 495 (MLCT).

Preparation of Metallo-Supramolecular Polymer

The polymer film onto conductive surface was obtained by electropolymerization of [Ni_2(*bisalphen*)] complex in THF/0.1 mol L^{-1}TBAP (under a nitrogen atmosphere) by cyclic voltammetry between 0.0 to 1.4 V *versus* SCE. The scan rate (15 mV s^{-1} to 150 mV s^{-1}), potential cycle number (3 to 5 cycles) and the monomer concentration (0.1 mmol L^{-1} to 1.0 mmol L^{-1}) were evaluated for polymeric film formation. Visual inspection of the platinum surface showed the deposition of dark orange film.

Electrochemical Behavior

In each electropolymerization study, the electrochemical behavior was investigated in 0.5 mol L^{-1} KCl solution by differential pulse voltammetry (pulse of 50 mV and scan rate of 5 mV s^{-1}). All measurements were carried out with continuous flow of nitrogen gas. The voltammograms were used to calculate of the electroactive surface coverage Γ (mol cm^{-2}), ensuring that the oxidation/reduction processes could occur on the whole film. The anions (Cl^-, ClO_4^-, NO_3^-, SO_4^{2-}) and cation (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}) influence was studied in aqueous solution with 0.5 mol L^{-1} concentration. The pH effect using universal buffer solution (1.0 to 10.0) containing 0.5 mol L^{-1} KCl as supporting electrolyte was also investigated.

RESULTS AND DISCUSSION

[Ni_2(*bisalphen*)] film formation by cyclic voltammetry

Initially, the poly[Ni_2(*bisalphen*)] was obtained in THF/0.1 mol L^{-1} TBAP by cyclic voltammetry between 0.0 to 1.4 V *versus* SCE at 100 mV s^{-1} with 15 polymerization cycles (Fig. 1). The fast mechanism of electropolymerization was similar to mechanism observed to classical *salen*[22,23], since the *Bisalphen* complexes should have as two independents *salen* unit, due to presenting a weak conjugation through the bridge[18,24]. However, two important step were observed for poly[Ni_2(*Bisalphen*)] formation in THF solvent, as illustrate in Fig.1 (insert). The first potential cycle showed an increase of anodic current in 1.0 V *versus* SCE, ascribed to the radical formation, in according to studies of the Aubert *et al.*[18]. In the first potential cycle, one cathodic peak in 0.69 V *versus* SCE was also observed ascribed to reduction of Ni^{III} to Ni^{II} present on polymeric structure formed[25]. The second potential cycle showed one redox couple (E_{pa} = 0.87 V e E_{pc} = 0.67 V *vs.*SCE), ascribed to redox couple Ni^{II}/Ni^{III} of polymeric film. The other potential cycles applied keeping the growth of polymer on electrode surface. The current responses to subsequent potential cycles decrease progressively after four cycles. This can be ascribed to formation of an electroactive film which impedes the diffusion of free monomers to the electrode surface and consequently decreases the oxidation of additional monomer for polymer formation.

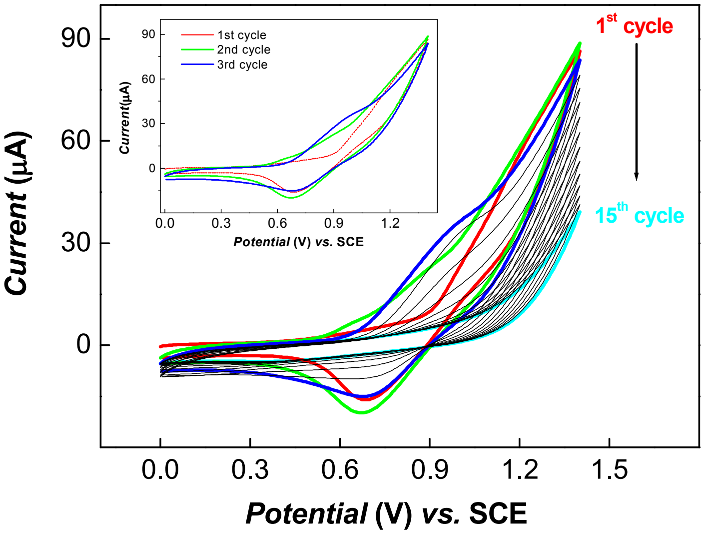
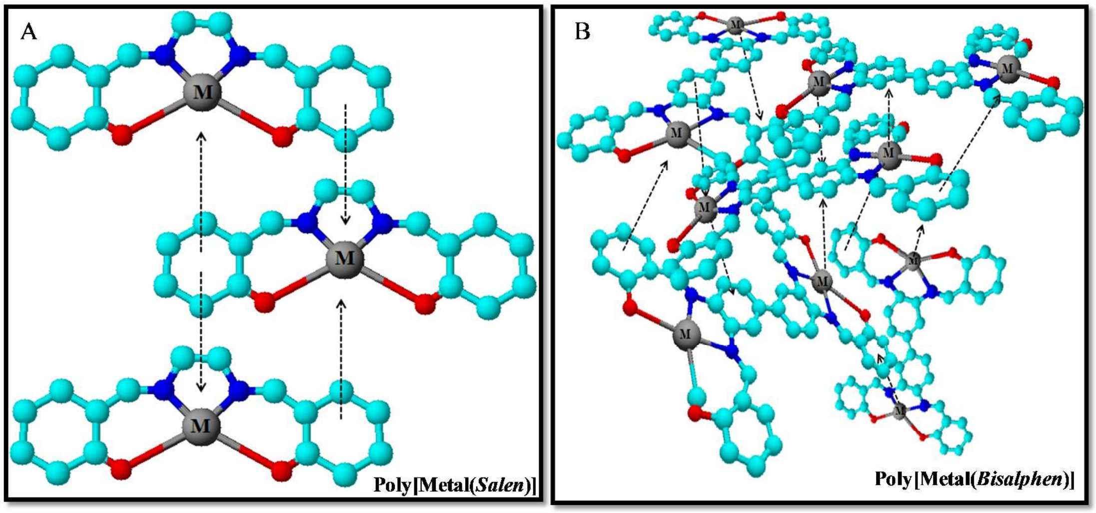


Fig. 1 Cyclic voltammogram of the electropolymerization stage to 1.0 mmol L^{-1} of [Ni$_2$(*bisalphen*)] complex in THF/0.1 mol L^{-1} TBAP using platinum electrode applying 15 potential cycles between 0.0 V to 1.4 V *vs*. SCE at 100 mV s^{-1}. Insert: Cyclic voltammogram to three first potential cycle of the electropolymerization.

The mechanism of the electro-oxidative polymerization of the complex still remains unclear. However, according to the previously reported data on the anodic oxidation of metal-salen complexes[4-7,26], the polymerization corresponds to the electron transfer from predominantly ligand-centered orbitals. The results corroborate the hypothesis that the model for the structure of poly(metal-*Schiff*) on the electrode surface is the generation of stacked polymer complexes (charge transfer complexes) formed due to the donor–acceptor interaction between the ligand of one monomer fragment and the metal center of another. Thus the supramolecular aggregates are not formed without oxidation of the central metal and/or correct orientation of the ligand and the metal center. Thus, the supramoleculares blocks are dependent on the interaction between the d bonding orbitals of the metal centers with π orbital of aromatic rings of the adjacent molecules.

The difference in electropolymerization profile and stability of polymer film formed can be related to the physical and chemical properties of solvent used in electropolymerization stage. Solvents used in this study were THF and DMF. This selection was based on the high solubility of the complex in these solvents. In DMF solvent, the formation of the polymeric film on the electrode surface was not observed. This solvent has a high viscosity (0.802 cP)[25] and influence directly in the process of diffusion of the monomer species to the electrode surface. The dipole moment can be related to maintaining radical cation in solution. When the lower dipole moment (1.75 μ to THF), higher be stability of radical cation in solution, as a result, a great amount of radical-radical attack may occur, favoring the formation of large polymer chains. This way, the poly[Ni_2(*bisalphen*)] formed in THF showed different voltammetric profiles for electropolymerization stage and better stability in aqueous solution.

In the studies of the Vilas-Boas and coworkers[6,26] were concluded that the poly-*salen* behaves like a polyphenylene compound, where the metal ion acting as a bridge between biphenylene moieties. Thus, the polymeric structure is formed by interaction of dπ molecular orbital of metal center with the π molecular orbital of aromatic ring of the adjacent monomers. Consequently, the metal cation does have a contribution in the π-delocalized system responsible for the charge conjugation[6,26]. The same behavior was observed to poly[Ni_2(*bisalphen*)], but the structural organization was not uniform like to polymers formed from classic *salen* complexes. Due to morphology changes of the monomer resulting from weak conjugation through the bridge, the polymeric structures were formed in clusters, which the blocks are formed from supramolecular structures. The schematic comparison of film structure of *salen* and *bisalphen* was illustrated in the Scheme 2.



Scheme 2. Comparison of polymeric film structure from a) metal-*salen* and b) metal-*bisalphen* complexes. Colors: cyan = carbon; blue = nitrogen; red = oxygen; gray = transition metal.

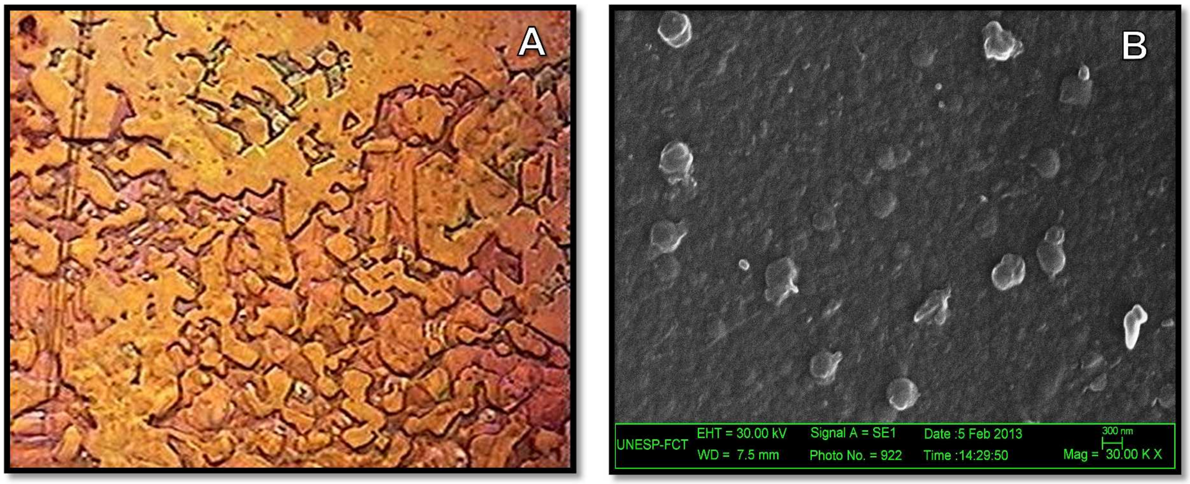


Fig. 2A) The images of optic microscopy (magnification – 500X), obtained to surface of platinum coated with the poly[Ni_2(*bisalphen*)] and B) scan electronic microscopy (SEM) (magnification – 30000X), obtained to surface of ITO coated with the poly[Ni_2(*bisalphen*)]. The polymer was formed in the same conditions for both surfaces.

The images of optic microscopy (Fig. 2A) and scanning electron microscopy (SEM) (Fig. 2B) obtained to surface of platinum coated with the poly[Ni_2(*bisalphen*)] show many cluster along the polymeric film, indicating the polymer film was formed supramolecular blocks.

Influence of electrochemical parameters

The formation of polymeric film can be influence by electrochemical parameters used in the electropolymerization stage, such as potential cycle number and scan rate. The monomer concentration can also influence in the polymer formation. The number of the potential cycle applied in the electropolymerization stage is related with the amount and/or size of the supramolecular blocks structure formed into conductive surface. This study was carried out to 1.0 mmol L^{-1} Ni_2(*bisalphen*) in THF/0,1 mol L^{-1} TBAP varying from 3 to 50 potential cycles. All polymeric films were obtained between 0.0 V to 1.4 V *versus* SCE at 100 mV s^{-1}. The cyclic voltammograms obtained in the electropolymerization stage showed the same behavior, where the first two potential cycles are crucial for the polymeric formation. However, the polymeric film growth was nonlinear with the number of applied cycles (Supplementary material – S1). Adsorbed molecules at the electrode surface are described by the surface coverage and that peak current becomes linear with concentration in the thin layer. In this study, the peak current of the electrode coated with poly[Ni_2(*bisalphen*)] depends sigmoidally on number of layers deposited. This characteristic can be ascribed to building of the supramolecular blocks is dependent of molecular structure. Thus, due to weak conjugation through the bridge and amount of aromatic ring present in the monomeric structure, the *bisalphen-type* complexes show great structural flexibility to formation of polymeric film through to supramolecular building blocks. The blocks can also be observed by the image obtained from AFM, which show big structures in nanometer size (Fig. 3).

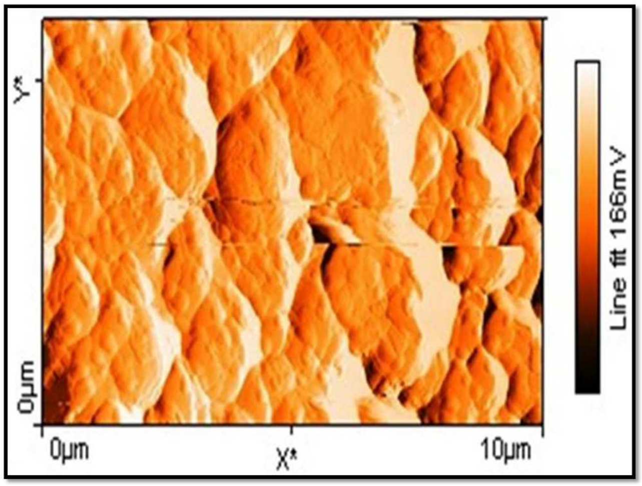


Fig. 3 AFM image of surface of ITO coated with the poly[Ni_2(*Bisalphen*)].

Due to these properties, the scan rate applied in the electropolymerization can be influence the polymer formation onto electrode surface. In the literature, Jian-Ling and coworkers[27] described the scan rate effect (5 mV s^{-1} to 150 mV s^{-1}) in anodic polymerization of Ni-*salen* complex. Their studies proved that growth rate of polymeric film increase for low scan rate values, where the best results were obtained at 20 mV s^{-1}. High scan rate values influence directly in the diffusion kinetic of monomer from solution to electrode surface, causing the decrease of monomer concentration in conductor surface and consequently a decrease in the polymer film formed[27]. On the other hand, the surface coverage of [Ni_2(*bisalphen*)] was nonlinear with the scan rate used in the electropolymerization stage (Supplementary material – S2). This can be ascribed to structural flexibility of *bisalphen* ligand. This way, the subsequent studies were carried out at moderate scan rates and potential cycles to try to establish a more uniform structure to the polymer.

The monomer concentration was also evaluated to understand the electropolymerization stage. The study was performed in THF/0.1 mol L^{-1} TBAP solution, in the range of 0.05 mmol L^{-1} to 1.0 mmol L^{-1} monomer concentration. Concentrations higher than 1.0 mmol L^{-1} were not analyzed due the solubility of monomer in the solvent. The increase of surface coverage (Γ = mol cm^{-2}) with the increase of monomer concentration was observed, as showed in the Fig. 4.

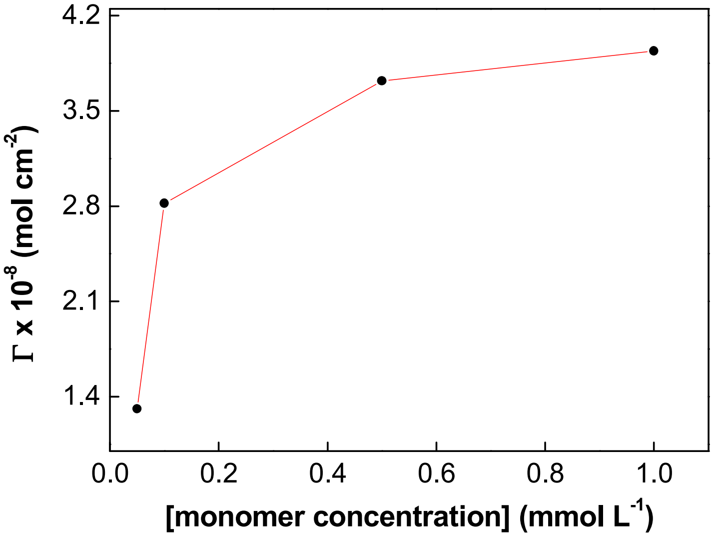


Fig. 4 Surface coverage values (mol cm^{-2}) calculate to poly[Ni$_2$(*bisalphen*)] in aqueous solution in function of the monomer concentration used in the electropolymerization stage.

The 0.5 mmol L^{-1} concentration monomer was sufficient to achieve maximum surface coverage of the poly[Ni$_2$(*bisalphen*)] onto platinum surface. Besides, the high concentration of Ni$_2$(*bisalphen*) complex provides the agglomerates formation in solution, which decrease the radical cation formation, consequently, decreasing the amount of film formed at each scanning cycle. On the other hand, moderate concentrations allow the electrogeneration of the radical cations and the formation of thicker films.

Electrochemical Behavior of poly[Ni$_2$(*bisalphen*)] in Aqueous Solution

The electrochemical behavior of poly[Ni$_2$(*Bisalphen*)] in aqueous solution was evaluated in 0.5 mol L^{-1} KCl solution at 5 mV s^{-1} by differential pulse voltammetry between -0.70 V to 0.80 V *vs.*

SCE with 50 mV of the pulse. The Fig. 5 shows the voltammograms obtained to platinum surface coated with the poly[Ni$_2$(*bisalphen*)] to anodic process. The voltammetric profile for the poly[Ni$_2$(*bisalphen*)] formed with 3 potential cycles showed just one redox process ($E_{pa}^{(peak\ I)}$ = -183 mV) ascribed to Ni^{I}/Ni^{II} redox couple. On the other hand, the poly[Ni$_2$(*Bisalphen*)] formed with 15 cycles showed three redox process. The peak I and II ($E_{pa}^{(peak\ I)}$ = -371 mV and $E_{pa}^{(peak\ II)}$ = -42 mV) can be ascribed to Ni^{I}/Ni^{II} redox couple and the peak III ($E_{pa}^{(peak\ III)}$ = 600 mV) can be ascribed to Ni^{II}/N^{iIII}.

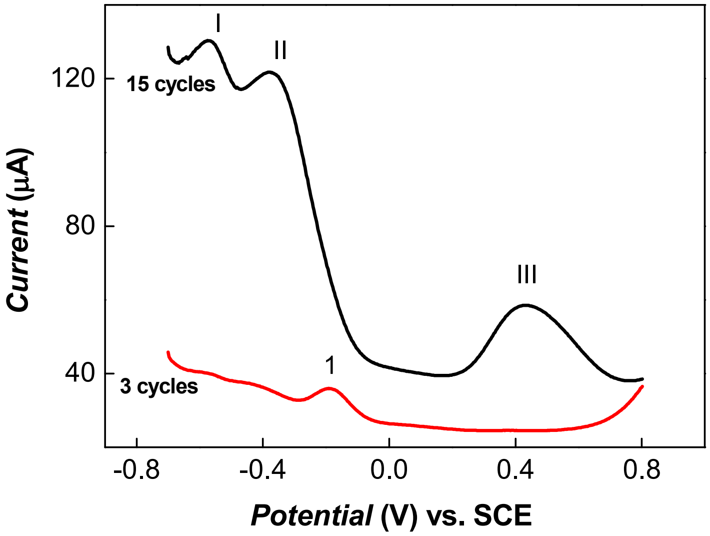


Fig. 5 Differential pulse voltammograms of poly[Ni$_2$(*bisalphen*)] modified electrode formed with 3 and 15 potential cycles. The electrochemical behavior was investigated in 0.5 mol L^{-1} KCl solution absence oxygen by differential pulse voltammetry (pulse of 50 mV and scan rate of 5 mV s^{-1}).

This behavior can be ascribed to orbital overlap deriving the molecular organization of the polymeric film provides two oxidation potentials for the same oxidation state of the metal center, and may be associated with the comproportionation effect. An important observation is that the higher supramolecular blocks formed in the electropolymerization stage, the great the comproportionation effect. Thus, more clustered structures provide a great overlap of orbitals and in consequence great possibility of electronic transfer process from polymeric film to electrode surface. This electronic communication is generated by overlapping dπ orbital of metallic center with π orbital of the ligand, making the unpaired electron of the metal acts as oscillating load during the redox process. Whereas a mechanism involving two electrochemical steps, the binuclear supramolecular complex may be represented by:

$$\mathrm{Ni^{II}(d\pi^{8})\text{-}L\text{-}(d\pi^{8})Ni^{II}} \xrightarrow{+e^{-}} \mathrm{Ni^{II}(d\pi^{8})\text{-}L\text{-}(d\pi^{9*})Ni^{I}} \qquad (E_1)$$

$$\mathrm{Ni^{II}(d\pi^{8})\text{-}L\text{-}(d\pi^{9*})Ni^{I}} \xrightarrow{+e^{-}} \mathrm{Ni^{I}(d\pi^{9})\text{-}L\text{-}(d\pi^{9})Ni^{I}} \qquad (E_2)$$

where "*" represents the unpaired electron which performs in the electronic delocalization during the redox process, L is ligand and E_1 and E_2 were reduction potentials.

Due to the increased possibilities of application of the electrocatalytic effect provided by comproportionation effect, the parameter of comproportionation effect (K_c - comproportionation constant and ΔG^o - Gibbs energy) were calculated to platinum surface coated with the poly[Ni_2(*bisalphen*)]. The electropolymerization was carried out to 1.0 mmol L^{-1} of monomer in THF/0.1 mol L^{-1} TBAP applying 15 potential cycles at 50 mV s^{-1}, and the electrochemical behavior was obtained in 0.5 mol L^{-1} KCl solution at 5 mV s^{-1} (Fig. 5). The comproportionation constant can be calculated by Equation 1[28, 29]:

$$K_c = exp\left(\frac{\Delta E_{1/2}}{25.69\ mV}\right) \qquad (1)$$

where $E_{1/2}$ with mV unit. This equation can be applied when the process redox involve only one electron. Thus, the K_c was calculated to Ni^{I}/Ni^{II} redox couple. The calculations showed a comproportionation constant of 8.86 x 10^3 in KCl solution, ascribed to system moderate coupling[30, 31]. This comproportionation constant value is in agreement with formation of polymeric film by interaction and not by effective bond.

This way, the Gibbs free energy can be calculated by:

$$\Delta G^{\circ} = -R\,T \ln K_c \tag{2}$$

Through this relation, the electronic transitions can display a character or exergonic ($\Delta G^0 < 0$, thermodynamically favorable) or endergonic (and $\Delta G^o > 0$, thermodynamically unfavorable), where species donors or recipients of electrons that make up the system must be chemically or electrochemically distinct. This difference is necessary for a change in energy during the electron transfer process occurs. Thus, in presence of potassium ion in solution, the poly[Ni_2(*bisalphen*)] presented a system thermodynamically favorable with ΔG^o equivalent to -22.52 kJ mol^{-1}.

Counterion effect

The repulsive force must also be present in the poly[Ni_2(*bisalphen*)] structure, that would impose an flexible structure. This way, the movement of species from solution into the film is necessary and can be associated with the polymer charge transfer[32]. Therefore, the counter ion effect as realized to understand the stability of poly[Ni_2(*bisalphen*)] in aqueous solution. The platinum coated with the poly[Ni_2(*bisalphen*)] was evaluated in various supporting electrolytes with different anions such as: Cl^-, NO_3^-, ClO_4^-, HSO_4^-, but similar cation (sodium ion) of 0.5 mol L^{-1} concentration. The same way, the influence of different cation (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} and Ba^{2+}) on electrochemical behavior of the polymeric film was studied. The solutions were prepared with similar anion (chloride ion) of 0.5 mol L^{-1} concentration. The great dependence of anion present in solution was observed to Ni^{II}/Ni^{III} redox potential (see Fig. 6). Although there has been an influence on the comproportionation effect, however the potentials of Ni(I) were almost always kept. It can be seen that the maximum current potential in the presence of various anions have same potential level. The average peak potential for Ni(I) is shown in dot line in Fig. 6.

The anion influence on the Ni^{II}/Ni^{III} redox couple may be related to a stabilization of the positive charge of the polymer, when the Ni(III) is formed by anodic scan. The results indicate that anion in solution induces in the redox couple in the follows the order: Cl^{-} (0.429 V) < HSO_4^{-} (0.544 V) < NO_3^{-} (0.604 V) < ClO_4^{-} (0.642 V) and shifted to more anodic values with the increase in ionic radium[33] of the anion. This same behavior was observed for polymers derived from classics *salen* polymers[4].

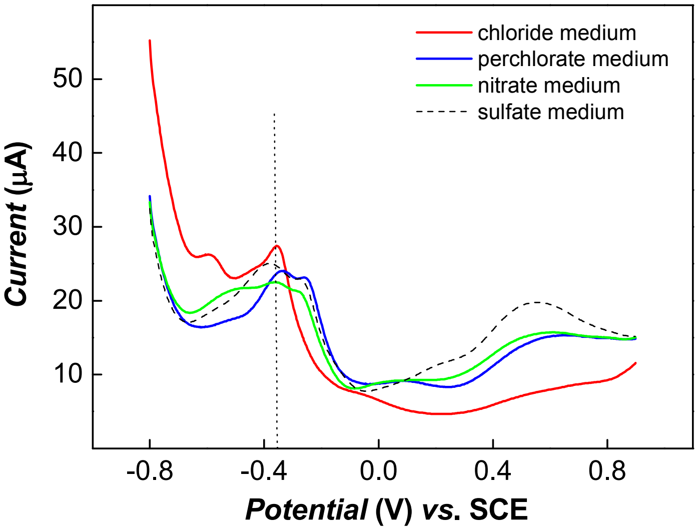


Fig. 6 Differential pulse voltammogram of poly[Ni_2(*bisalphen*) modified electrode in presence of different anions (ClO_4^-, Cl^-, NO_3^-, HSO_4^-) at 0.5 mol L^{-1}. (pulse = 50 mV; scan rate = 5 mV s^{-1}).

In the same way, the cation influence on the the Ni^{I}/Ni^{II} redox couple (Supplementary material – S3), may be related to a stabilization of the negative charge of the polymer, when the Ni(I) is formed by cathodic scan. We can conclude that anions showed influence of redox processes in Ni(II)/Ni(III) and cations influence of redox processes in Ni(I)/Ni(II), proving the relationship of formal charge generated in the processes of oxidation and reduction and the need to balance the charge of the complex ion.

pH effect

The pH study was conducted in universal buffer containing KCl 0.5 mol L^{-1} as supporting electrolyte. The pH range measured was 1.0 to 8.0. Two distinct regions were observed for the redox processes as a function of pH, where for low pH values lower than 4.0, a strong dependence on more negative potentials were observed, and can observe only the redox processes ascribed to Ni^{I}/Ni^{II} redox couple (Fig. 7).

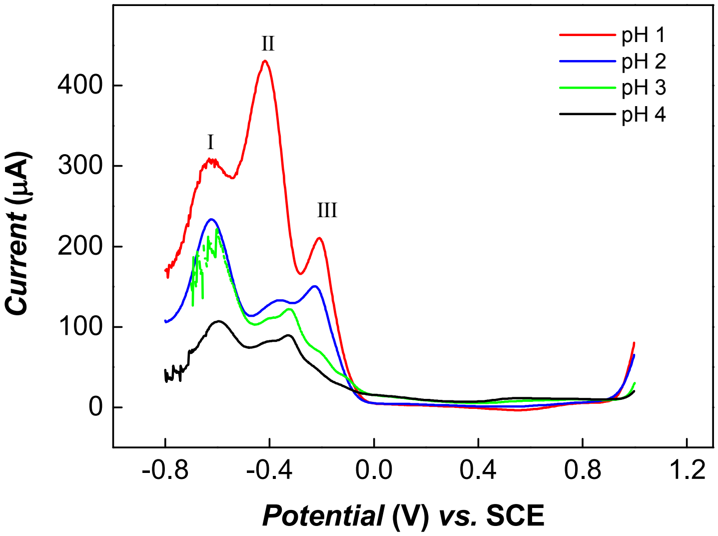


Fig. 7 Differential pulse voltammogram of poly[Ni_2(*bisalphen*) modified electrode evaluated in universal buffer and 0.5 mol L^{-1} KCl solution as supporting electrolyte between pH 1.0 and 4.0.

This profile change can be related to the hydrogen ion concentration of the medium. Higher the H^+ concentration of the medium, the greater the difficulty occurs Ni^{II}/Ni^{III} redox process, because the polymer don't have stability in presence of positive charge, which is consistent with studies observed in the study of the counter ion. Thus, to low pH values, the Ni^{I}/Ni^{II} redox process is favored. On the other hand, for higher pH values (above 5.0) the Ni^{I}/Ni^{II} and Ni^{II}/Ni^{III} redox processes were clearly observed (Fig. 8). This can be ascribed to the increased of concentration of the hydroxyl ions in the medium, which stabilize the polymer, when the positive charge if formed at oxidation of Ni^{II} to Ni^{III}. However, at pH 8.0 a possible formation of nickel(II) hydroxide ($Ni(OH)_2$) in the polymeric film may occur[34], consequently just one redox process was observed (-0.40 V).

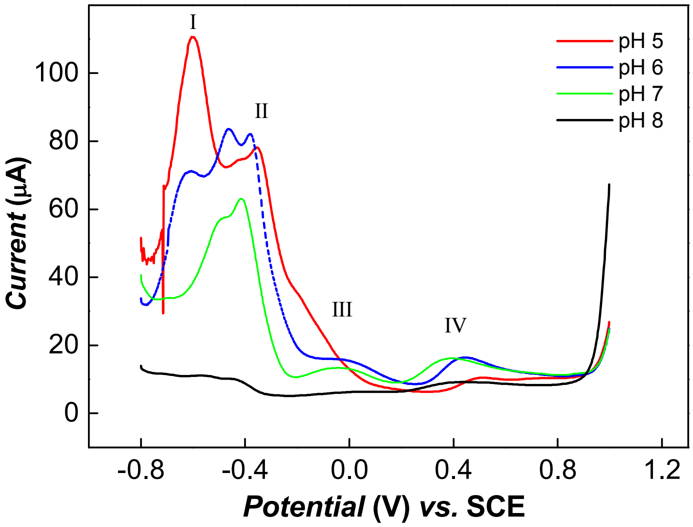


Fig 8. Differential pulse voltammogram of poly[Ni_2(*bisalphen*) modified electrode evaluated in universal buffer and 0.5 mol L^{-1} KCl solution as supporting electrolyte between pH 5.0 and 8.0.

Structural Characterization by Raman Spectroscopy

The poly[Ni_2(*bisalphen*)] obtained onto platinum surface was analyzed by Raman spectroscopy. The Fig. 9 shows the Raman spectrum (excitation 633 nm) obtained both to poly[Ni_2(*bisalphen*)] and Ni_2(*bisalphen*) solid monomer, which showed a similar spectrum. This characteristic indicates that the structural conformation of the polymer did not alter the main structure of the monomer, where the increased intensity of peaks can be ascribed to clusters generated and as a result of the stretching magnification of the signal at certain frequencies[35].

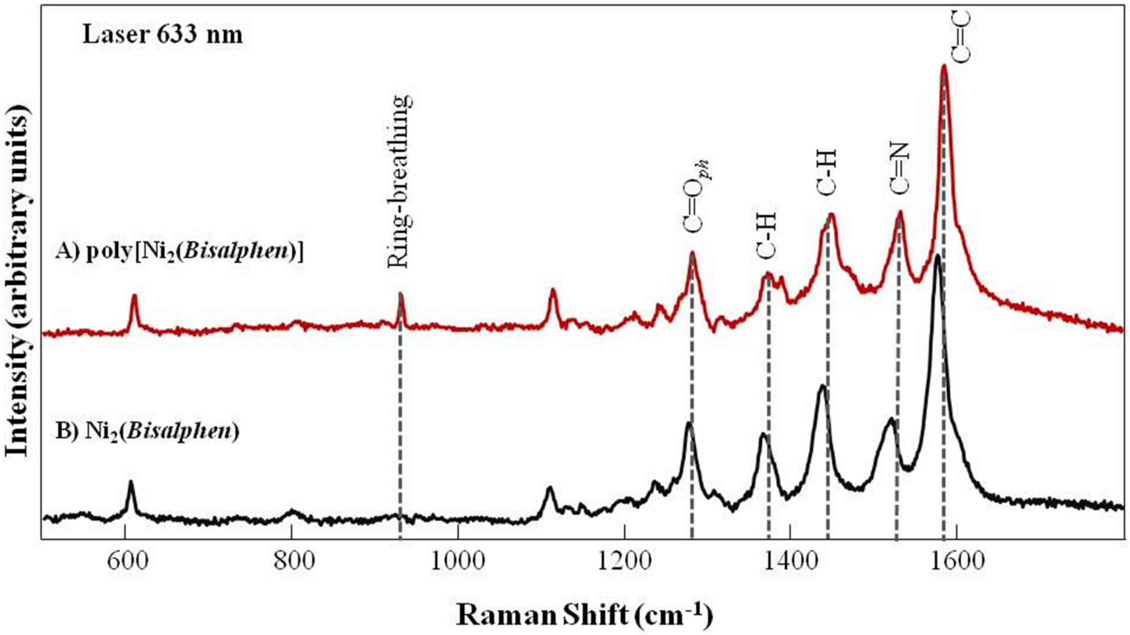


Fig. 9 Raman spectrum for the a) poly[Ni$_2$(*bisalphen*)] onto platinum electrode surface and b) Ni$_2$(*bisalphen*) solid monomer (laser 633 nm).

When compared the poly[Ni$_2$(*Bisalphen*)]with the Ni$_2$(*Bisalphen*) Raman spectrum, a shift of bond frequency to lower values were observed. This change can be ascribed to interaction among the monomers present in each layer of polymer. The principal change was observed to C=C (1576 cm^{-1} → 1583 cm^{-1}), C=N (1518 cm^{-1} → 1531 cm^{-1}) and C–O$_{ph}$ (1277 cm^{-1} → 1281 cm^{-1}) stretching, which confirm a formation of polymer by the interaction of aromatic ring and the coordination center (N$_2$O$_2$) of *Schiff* ligand[4,6,26]. The frequency shift and intensity decrease of the C–H out of plane deformation (1365 cm^{-1} → 1388 cm^{-1}) was also observed. This can be ascribed to decrease of vibration out of plane due to layers formation (molecular columns). In addition, a new band in 931 cm^{-1} ascribed to ring-breathing was observed just to poly[Ni(*bisalphen*)] spectrum, which may be associated with cluster vibration.

CONCLUSION

The poly[Ni_2(*bisalphen*)] formation by electropolymerization is directly influenced by solvent, which keeping the radical cation in solution to reaction propagation. The supramolecular building blocks are formed by interaction between metal cation and aromatic ring similar to the classical *salen* polymer. However, the weak conjugation through the bridge allows the formation of clusters structures. Thus, the polymeric film showed supramolecular blocks, which have characteristics of their monomer units. These characteristics make these polymer versatile materials, in particular to application as sensor, in electrocatalysts and energy storage system.

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Author Contributions

The manuscript was written through contributions of all authors.

Funding Sources

São Paulo Research Foundation (FAPESP)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors are thankful to Foundation for São Paulo Research Foundation - FAPESP(2010/12524-6 and 2013/10469-6) by the scholarship granted to C. S. Martin and W. B. S. Machini, respectively.

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