

Tetracyanoquinodimethanide adsorbed on a silica gel modified with titanium oxide for electrocatalytic oxidation of hydrazine

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Abstract The electrocatalytic oxidation of hydrazine at low potential using tetracyanoquinodimethanide adsorbed on silica modified with titanium oxide was investigated by cyclic voltammetry and amperometry. The modified electrode was prepared modifying a carbon paste electrode employing lithium tetracyanoquinodimethanide adsorbed onto silica gel modified with titanium oxide. This electrode showed an excellent catalytic activity and stability for hydrazine oxidation. With this modified electrode, the oxidation potential of hydrazine was shifted toward less positive value, presenting a peak current much higher than those observed on a bare GC electrode. The linear response range, sensitivity and detection limit were, respectively, 2 up to 100 $\mu\text{mol l}^{-1}$, 0.36 $\mu\text{A l}^{-1}$, and 0.60 $\mu\text{mol l}^{-1}$. The repeatability of the modified electrode evaluated in term of relative standard deviation was 4.2% for 10 measurements of 100 $\mu\text{mol l}^{-1}$ hydrazine solution. The number of electrons involved in hydrazine oxidation (4), the heterogeneous electron transfer rate constant ($1.08 \times 10^3 \text{ mol}^{-1} \text{ l s}^{-1}$), and diffusion coefficient ($5.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) were evaluated with a rotating disk electrode.

Keywords Hydrazine · Modified electrode · LiTCNQ

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Introduction

Hydrazine (N_2H_4) is a strong reducing agent used as oxygen scavenger for corrosion control in boilers and hot-water heating systems [1]. It is also employed as starting material for many derivatives such as foaming agents for plastics, antioxidants, polymers, pesticides, plant-growth regulators, and pharmaceuticals [2].

Hydrazine also has been recognized as a neurotoxin, carcinogenic mutagenic, and hepatotoxic substance, which affects liver and brain glutathione [3]. It is therefore obvious that reliable and sensitive analytical methods for the determination of hydrazine are needed.

In this sense, many analytical methods have been developed for hydrazine determination, such as: spectrophotometric [4], fluorimetric [5], chemiluminescence [6], and chromatographic [7]. However, most of them suffer difficulties with sample preparation, its necessity of molecules derivatization, or lack of sufficient sensitivity, which limit their utility. In general, electrochemical methods present the advantages of simplicity and high sensitivity.

Electrochemical techniques have been shown to provide a sensitive and selective approach for the detection of numerous compounds. Unfortunately, hydrazine needs a large overpotential to be oxidized at ordinary electrodes, being unsuitable analyte for these methods [8]. Thus, the use of chemically modified electrodes containing selected redox mediators immobilized on conventional electrode surfaces has decreased the overpotential for hydrazine oxidation.

A wide variety of compounds has been used as electron mediators for hydrazine electrooxidation such as catechin film [9], hydroquinone salophen derivatives [10], iron-tetraaminophthalocyanine [11], dinuclear ruthenium phtha-

locyanine [12], cobalt phthalocyanine [13], cobalt phthalocyanine/cellulose acetate [14], iron phthalocyanine complex linked to mercaptopyrindine self-assembled monolayer [15], nickel hexacyanoferrate [16], zinc pentacyanonitrosylferrate film [17], nickel pentacyanonitrosulferrate film modified aluminum [18], hybrid hexacyanoferrates of copper and cobalt films [19], carbon nanotube [20], pyrogallol red [21], DNA [22], chlorogenic acid/carbon ceramic composite [23], etc. In most cases, the modified electrodes present low sensitivity, small range of linear response, poor detection limit, and/or low stability.

On the other hand, recent applications of a modified electrodes based on TCNX compounds (TCNE for tetracyanoethylene and TCNQ for tetracyanoquinodimethane) has been performed reaching a detectability at nanomolar level, with high stability, sensitivity, and large linear response range [24–26]. The TCNX compounds are good electron acceptor because its four cyan groups and the π conjugated system [27]. Indeed, these compounds present a high electronic affinity and a resonant system [28] that can promote a rapid electron transfer. The versatility of the silica gel surface in immobilizing many species, while retaining its general properties such as rigidity, porosity, particle size, high specific surface area, and chemical stability, makes it very attractive to immobilize electrons mediators for catalytic and electroanalytical purposes [29]. Silica gel chemically modified with titanium (IV) oxide presents a surface with amphoteric properties [30]. The cationic species on the surface can interact with anionic species permitting the use of this material to construct a modified electrode [31]. In this work, an efficient catalytic system employing a carbon paste electrode based on lithium tetracyanoquinodimethanide (LiTCNQ) adsorbed on silica titanium for the hydrazine oxidation at low potential. Therefore, the performance of the modified electrode for practical purpose was also investigated.

Materials and methods

Chemical and solutions

All solutions were prepared from analytical grade chemicals. Pipes [piperazine-*N,N'*-bis[2-ethanesulfonic acid]], Hepes [*N*-(2-hydroxyethyl) piperazine-*N'*-[2-ethanesulfonic acid]], and Tris [tris(hydroxymethyl)amino-methane] were acquired from Sigma, St. Louis, USA. Disodium phosphate (Na_2HPO_4) was acquired from Synth, São Paulo, Brazil. Tetracyanoquinodimethane (TCNQ) was acquired from Aldrich, Steinheim, Germany; lithium iodide (LiI) and hydrazine were acquired from Merck, Darmstadt, Germany. The synthesis of LiTCNQ was performed according to the literature [32].

Graphite powder (purity 99.9%) was supplied by Aldrich, Milwaukee, USA, mineral oil was acquired from Sheering-Plough, Kenilworth, USA and used to prepare the carbon paste. Silica gel was supplied by Fluka, Buchs, Switzerland, with an average pore diameter of 6 nm and particle size of 0.04–0.063 mm was used without further treatment. The solutions were prepared by using water purified in a Milli-Q Millipore system and the actual pH of the buffer solutions were determined with a Corning pH/Ion Analyser model 350.

Electrode preparation

An electrode with geometrical area of 0.2 cm² (5 mm diameter) was used for modified electrode construction. The preparation of silica–titanium (ST) was performed modifying the silica gel surface with titanium oxide according to the procedure described by Kubota et al. [33].

The adsorption of LiTCNQ on modified silica was carried out preparing a solution of 1 mmol l⁻¹ LiTCNQ in acetonitrile. After this step, 600 μl of this solution was added to 75 mg of ST under shaken. After 12 h, the resulting solid was filtered and washed for several times with acetonitrile, and then it was dried at 323 K for 30 min. This material will be denoted as tetracyanoquinodimethanide adsorbed on silica modified with titanium oxide (STTCNQ). Different concentrations of LiTCNQ were used to verify the adsorption profile. The modified electrode was prepared by mixing 10 mg of graphite, 10 mg of STTCNQ, and 15 μl of mineral oil, until a homogeneous paste is achieved. About 10 mg of this paste was transferred to the cavity of a home-made Teflon holder with an internal diameter of 5 mm and 1 mm deep using pyrolytic graphite in the bottom for the electric contact. The modified carbon paste electrode obtained in this study will be denoted as CPE/STTCNQ.

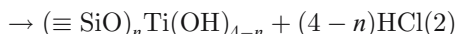
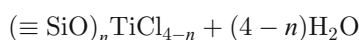
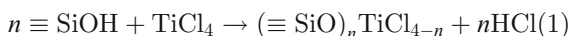
Electrochemical measurements

The voltammetric and amperometric measurements were carried out in a conventional three-electrode electrochemical cell. An SCE electrode and a coiled Pt wire were used as the reference and the counter electrode, respectively. Potentiostat PGSTAT30 Model from Echo Chemie (Utrecht, Netherlands) connected to a PC microcomputer for data acquisition and potential control was used for electrochemical measurement. A rotating disk electrode (RDE) (Pine Instrument, model 101 Industrial Drive, Grove City, USA) was used for the kinetic studies. The amperometric measurements were performed using a potential of 0.150 V vs SCE and a rotation rate of 23.56 rad s⁻¹. The measurements with the Rotating disc electrode (RDE) were carried out in a scan rate of 0.005 V vs SCE using different

rotation rate (23.56, 34.03, 41.89, 52.36, 64.45, 94.25, 167.55, and 261.80 rad s⁻¹). The measurements were carried removing the oxygen by bubbling nitrogen through the solution.

Results and discussion

The synthesis of ST was carried according to the procedure described by Kubota et al. [33]. The first step is based in the graft of TiCl₄ on the silica surface, and the second is based on the hydrolysis of remaining chloride, represented by the following equations [33]:



where (≡SiO)_nTi(OH)_{4-n} is denominated as ST. The quantity of ST grafted on surface of the material was 0.33 mmol g⁻¹ determined by X-ray fluorescence and the surface area was determined by BET method (294 m² g⁻¹) [34]. The adsorption of LiTCNQ on ST was carried out to obtain a maximum adsorption capacity.

Electrochemical behavior of STTCNQ and electrocatalytic oxidation of hydrazine

Figure 1 shows that cyclic voltammograms of the CPE (A) and CPE/ST (B) presented no faradic current, whereas for the CPE/STTCNQ (voltammogram C) a redox couple was observed with anodic and cathodic peaks at about 0.15 and 0.025 V, respectively. These peaks can be attributed to the

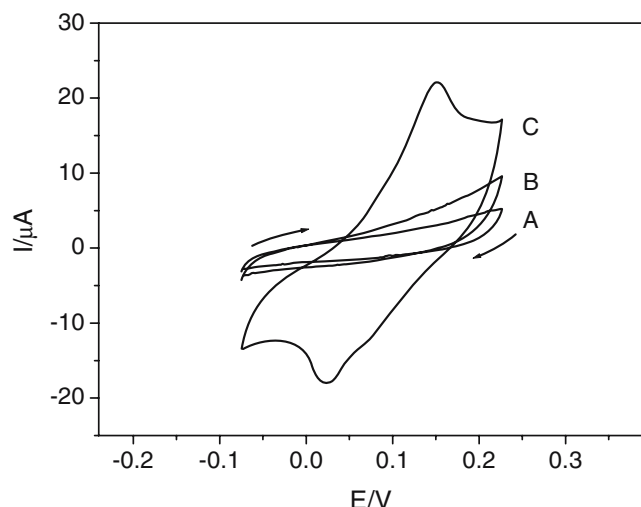


Fig. 1 Cyclic voltammograms obtained for: **a** CPE; **b** CPE/ST, and **c** CPE/STTCNQ in 0.1 mol l⁻¹ MacIlvaine buffer solution at pH 7.0 with a scan rate of 0.05 V s⁻¹

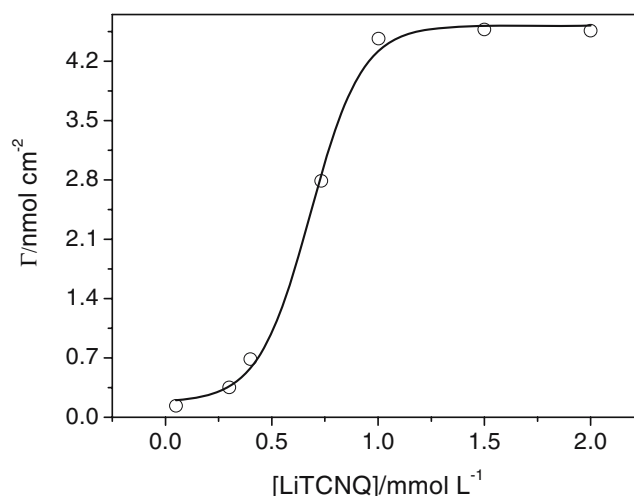


Fig. 2 Surface coverage obtained with CPE/STTCNQ prepared with ST in contact with different concentrations of LiTCNQ. These measurement were carried by cyclic voltammetry (CV) in: 0.1 mol l⁻¹ MacIlvaine buffer solution at pH 7.0 with a scan rate of 0.05 V s⁻¹

oxidation and reduction of the LiTCNQ species immobilized in ST. CPE/STTCNQ prepared using STTCNQ obtained from solutions with different concentrations of LiTCNQ was evaluated to find the maximum adsorption. Figure 2 shows the curve where the LiTCNQ concentration is sufficient to reach the maximum adsorption of LiTCNQ, for electrochemical purpose. It was evaluated integrating the area of the anodic wave of the cyclic voltammograms obtained at low scan rate for CPE/STTCNQ. The surface coverage with active catalysts Γ can be estimated from the relation $\Gamma = Q/nFA$, where Q is the charge obtained by integration the cathodic peak of the modified electrode in absence of hydrazine and the other symbols have their usual meanings. It is clear that for concentration of LiTCNQ higher than 1 mmol l⁻¹, the coverage remains almost constant at maximum capacity and, therefore, this concentration was used for further experiments.

Figure 3 shows the cyclic voltammograms recorded at pH 7.0 for CPE/STTCNQ in the absence (A) and in the presence of 1 mmol l⁻¹ hydrazine (B). In the presence of hydrazine, the oxidation peak is enhanced in the same oxidation potential of the STTCNQ (0.15 V) revealing the electrocatalytic activity of LiTCNQ. These results indicate that the electrocatalytic activity of the modified electrode can be applied for hydrazine determination at low potential. This higher response can also be associated with the formation of the charge transfer complex intermediate between hydrazine and adsorbed LiTCNQ.

Influence of the graphite power and STTCNQ ratio

The influence of the ratio between graphite powder and STTCNQ used in the modified electrode preparation on the

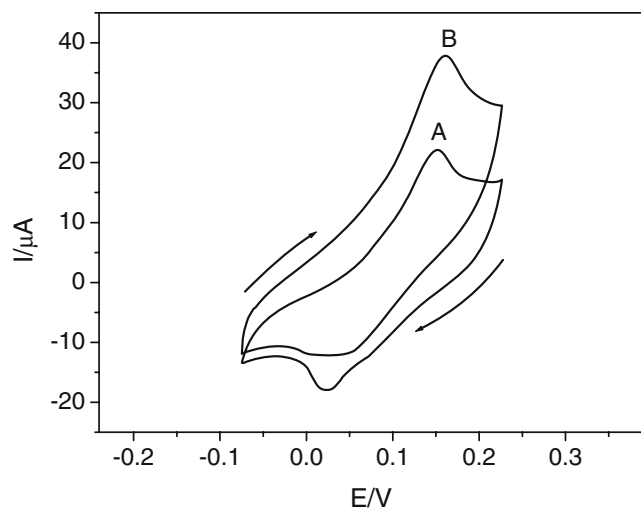


Fig. 3 Cyclic voltammograms obtained for CPE/STTCNQ in: **a** absence and **b** presence of 1.0 mmol Γ^{-1} hydrazine in 0.1 mol Γ^{-1} phosphate buffer solution at pH 7.0, with a scan rate of 0.05 V s^{-1}

peak current was investigated in the proportions 2:3, 1:1, 3:2, and 4:2 (*w/w*) in MacIlvaine buffer solution (pH 7.0) containing 100 $\mu\text{mol } \Gamma^{-1}$ hydrazine, with an oxidation potential of 0.15 V vs SCE. The results indicated that the best analytical signal was obtained using a proportion 1:1 (33.15 μA). Proportions lower and higher than 1:1 has not obtained a good homogenization of the carbon paste. Therefore, the response of the modified electrode were inferior (31.58 up to 32.42 μA).

Influences of pH, buffer, and buffer concentration

The effect of pH on the electrocatalytical oxidation of 100 $\mu\text{mol } \Gamma^{-1}$ hydrazine was studied in 0.1 mol Γ^{-1} MacIlvaine buffer solutions of different pH (5.5, 6.0, 6.5, 7.0, 7.5, and 8.0). The results show that the peak current increased with pH in the range from 7.0 up to 8.0 (33.8 μA) and for pH values lower than 7.0 the current decrease (32.25 μA). Thus, the optimum pH for further studies was fix at 7.0.

The effect of the supporting electrolyte on the modified electrode response was tested in 0.1 mol Γ^{-1} MacIlvaine (33.33 \pm 0.05 μA), phosphate (35.05 \pm 0.03 μA), Pipes (31.19 \pm 0.08 μA), and Hepes (30.76 \pm 0.10 μA) buffer solutions. The results indicated that phosphate buffer solution gives the best response. In addition, measurements carried out with different concentrations of phosphate, varying from 0.025 up to 0.2 mol Γ^{-1} presented almost constant response for concentrations in the range from 0.1 up to 0.2 mol Γ^{-1} (35.01 \pm 0.07 μA). In this sense, the concentration 0.1 mol Γ^{-1} was chosen for the further experiments. For concentration lower than 0.1 mol Γ^{-1} , the response decrease probably due to the resistance of the solution.

Kinetic studies of the hydrazine oxidation on the CPE/STTCNQ

Additional information about hydrazine oxidation on the modified electrode surface was obtained by analyzing the catalytic current from the cyclic voltammograms. According to Andrieux and Sev ant [35], a theoretical model for the catalytic current I_p depends on the potential scan rates v as follows:

$$I_p = 0.496FAC_o * D^{1/2}(Fv/RT)^{1/2} \quad (1)$$

where, C_o^* is the substrate concentration, D_o represents the diffusion coefficient of the substrate, F is the Faraday constant, R and T are the gas constant and temperature, respectively. Furthermore, a catalytic system behaves as a totally irreversible system controlled by diffusion for large values of kinetic parameters (i.e., large values of the

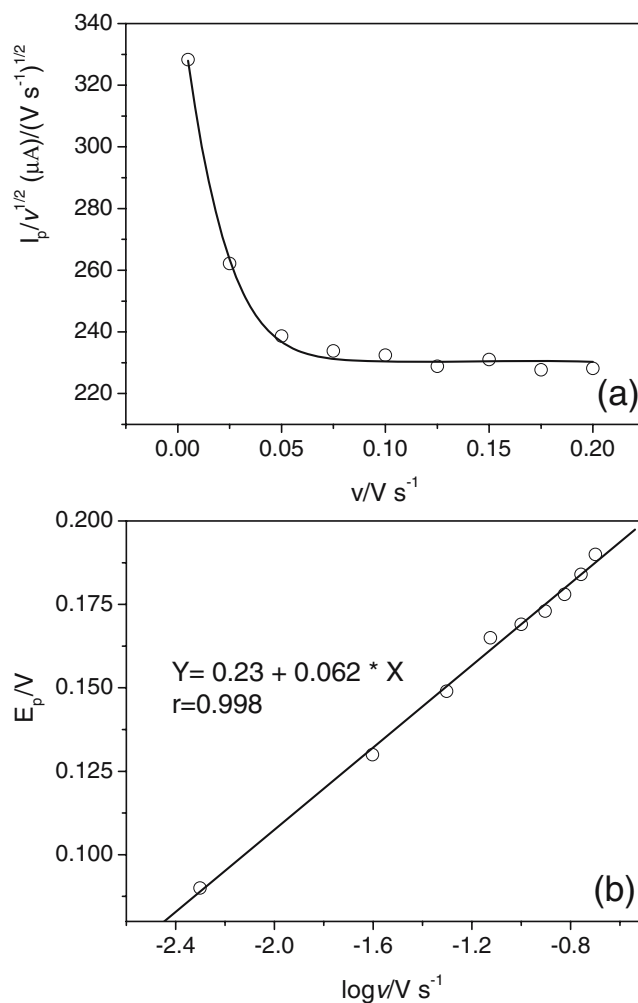


Fig. 4 Variation of the scan rate-normalized current ($I_p/v^{1/2}$) with scan rate on CPE/STTCNQ in solutions containing 500 $\mu\text{mol } \Gamma^{-1}$ hydrazine (**a**) and plot of the E_{pa} vs $\log v$ plot for hydrazine at the CPE/STTCNQ (**b**). All studies were performed in 0.1 mol Γ^{-1} phosphate buffer at pH 7.0. Scan rate 0.025–0.200 V s^{-1}

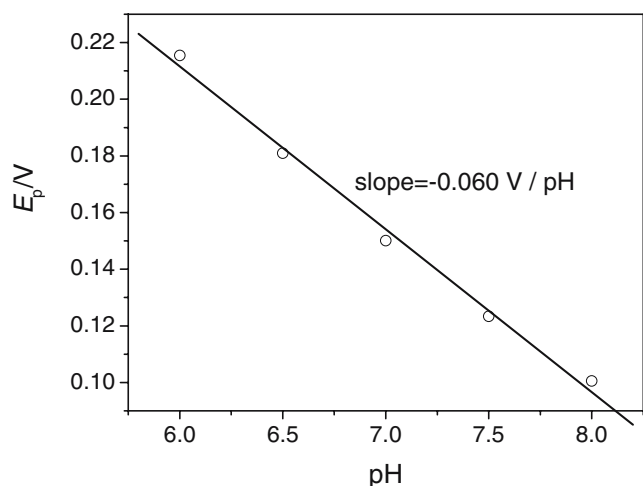


Fig. 5 Influence of pH on the peak potentials obtained by CV in solution containing $100 \mu\text{mol l}^{-1}$ hydrazine in 0.1 mol l^{-1} MacIlvaine buffer at pH 7.0, with scan rate of 0.05 V s^{-1}

catalytic rate constant, k) [35, 36]. First, a plot of the catalytic current I_p vs the square root of the potential scan rate, $\nu^{1/2}$, was plotted and resulted in a straight line ($Y = 8.14 + 207.39X$), suggesting that the process is controlled by mass transport. Second, a plot of the sweep rate-normalized current $I_p/\nu^{1/2}$ vs the sweep rate (Fig. 4a), exhibited the characteristic shape of a typical EC_{cat} process [36].

As can be seen in Fig. 3, in presence of hydrazine, an increase in the anodic peak and a decrease in the cathodic peak are observed in the cyclic voltammogram and these were found to be dependent on the scan rate, as expected for a totally irreversible process. Thus, the number of electrons n involved in the overall reaction can be obtained from the slope of the j_p vs $\nu^{1/2}$ plot according to the equation for a totally irreversible process controlled by diffusion [36]:

$$I_p = (2.99 \times 10^5)n[(1 - \alpha)n_a]^{1/2}AC_o * D_o^{1/2} \nu^{1/2} \quad (2)$$

where α is the electron transfer coefficient, n_a represents the number of electrons involved in the rate-determining step, D_o ($\text{cm}^2 \text{ s}^{-1}$) and C_o^* (mol cm^{-3}) the diffusion coefficient and the concentration of the electroactive species, respectively, and the other terms with their meanings mentioned before. In the present study, the values of the concentration and diffusion coefficient used for hydrazine in aqueous solution were $5 \times 10^{-7} \text{ mol cm}^{-3}$ and $6.28 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [16], respectively. In addition, considering that the $[(1-\alpha)n_a]$ value has to be known, one approach was employed for the hydrazine oxidation reaction based on the dependence of the peak potential E_{pa} with $\log \nu$ plot (Fig. 4b). For an irreversible reaction, the change in E_{pa} for each tenfold increase in ν is given by $1.15 RT/[(1-\alpha)n_a]F$ [36]. From the slope 0.062 V/decade , the values of $[(1-\alpha)n_a]$ was calcu-

lated as being 0.48. Thus, using this value in Eq. (2) and the slope $207.39 \mu\text{A}/(\text{V s}^{-1})^{1/2}$ extracted from plot I_p vs $\nu^{1/2}$, the value of n was calculated being 4.0, in direct agreement to others works based on the catalytic oxidation of hydrazine utilizing others modifier [19, 37, 38].

After that, to verify the chemical order of protons of the electrooxidation of hydrazine an analysis of the dependence of E_p (peak potential) vs pH was performed (Fig. 5) and was observed that the peak potential was dependent of the solution pH. A linear correlation obtained from pH 6.0 up to 8.0 for E_p vs pH curve with a slope of 0.06 V/pH , is close to that expected for a monoelectronic/monoprotonic electrode reaction which is 0.059 V/pH at $25 \text{ }^\circ\text{C}$. Thus, the number of protons involved in this process should be equal to electrons number, or $0.059 (n_p/n_e) \text{ V/pH}$ where $n_p=n_e$ [39].

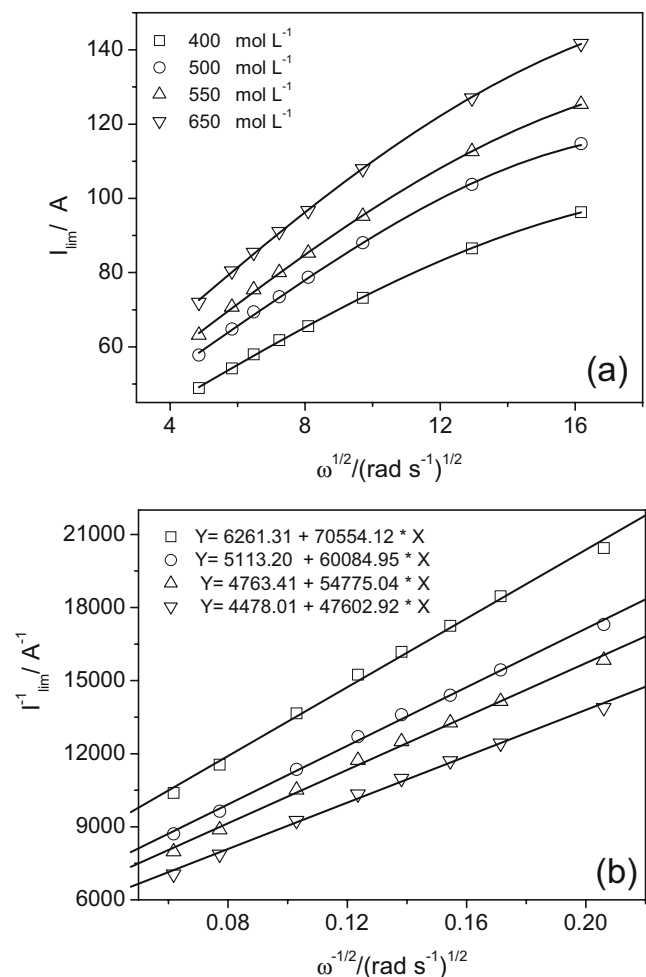


Fig. 6 Levich plot for the hydrazine oxidation on CPE/STTCNQ (a) and Koutecky–Levich plot for the modified electrode (b). This study was made in four different hydrazine concentrations (400, 500, 550, and $650 \mu\text{mol l}^{-1}$). All studies were carried with a scan rate of 0.005 V s^{-1} in 0.1 mol l^{-1} phosphate buffer at pH 7.0. Electrode rotation rates: 23.56, 34.03, 41.89, 52.36, 64.45, 94.25, 167.55, and $261.80 \text{ rad s}^{-1}$

Rotating disk electrode

Indeed, linear sweep voltammograms were recorded after obtaining the polarization curves for the hydrazine oxidation reaction at different electrode rotation rates ω (rad s^{-1}) and different hydrazine concentrations in phosphate buffer (pH 7.0). The limiting currents obtained on the modified electrode increased with rotation speed of the electrode and the linearity of the Levich plots at lower rotation rates indicates that the reaction is controlled by mass transport (Fig. 6a). On the other hand, a deviation from the linearity in the Levich plots was observed at higher rotation rates, suggesting kinetic limitations. For high values of rotation rate, the thickness of the Levich layer decreases and the magnitude of the current begin to be controlled by the rate of the redox-mediated reaction between hydrazine and STTCNQ. In such case, the polarization curves are more conveniently analyzed by means of Koutecky–Levich plots, where the currents for the hydrazine oxidation on the rotating disk electrode are analyzed in potential regions where kinetic and the mass transport contribution are related as follows [36]:

$$\frac{1}{I_{\text{lim}}} = \frac{1}{nFAC_0k_b\Gamma} + \frac{1}{0.62nFAD^{2/3}\kappa^{1/6}C_0} \times \frac{1}{\omega^{1/2}} \quad (3)$$

where k_b the rate constant ($\text{M}^{-1} \text{s}^{-1} = \text{mol}^{-1} \text{l s}^{-1}$) for the reaction between the catalyst and the hydrazine molecule, Γ , the quantity of the active catalyst on the electrode surface (mol cm^{-2}), and κ the kinematic viscosity of the aqueous solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$).

According to these equations, at a given potential, a plot of Γ^{-1} vs $\omega^{-1/2}$ should be linear (Fig. 6b) and the rate constant k_b could be calculated from the intercept. The values of k decreased as the bulk concentration of hydrazine increased and varied from 1.12×10^3 to $9.68 \times 10^1 \text{ mol}^{-1} \text{ s}^{-1}$ hydrazine concentrations between 400 to 650 $\mu\text{mol l}^{-1}$. In the present

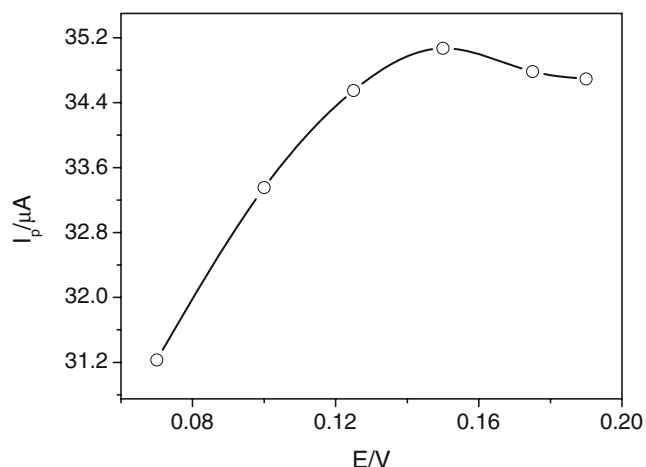


Fig. 7 Influence of the applied potential (0.070, 0.100, 0.125, 0.150, 0.175 and 190 V vs SCE) on the response of the modified electrode in 0.1 $\mu\text{mol l}^{-1}$ phosphate buffer (pH 7.0) containing 100 $\mu\text{mol l}^{-1}$

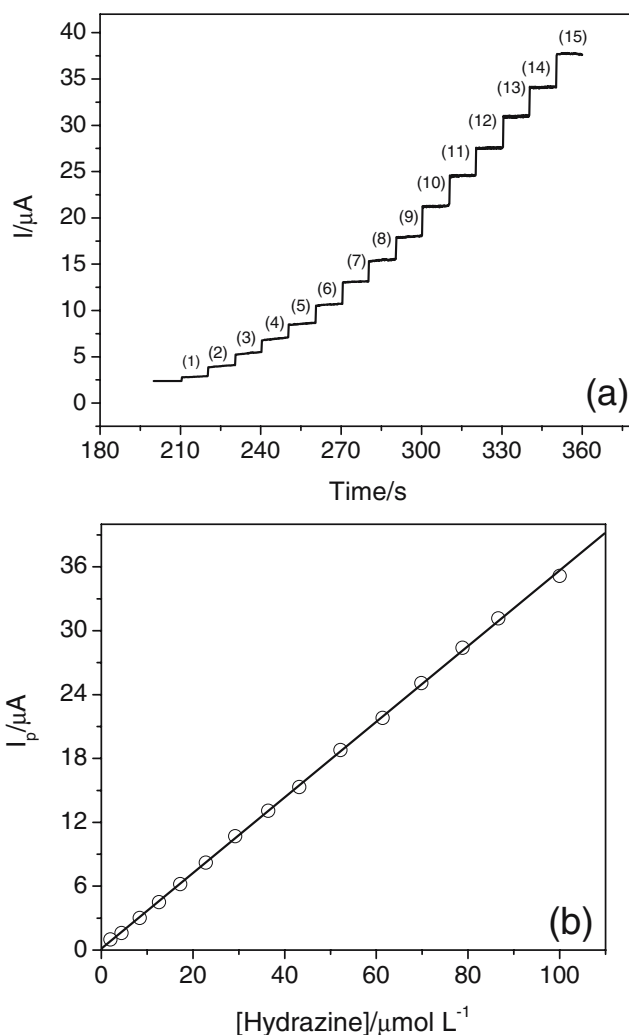


Fig. 8 Amperometric response for the hydrazine oxidation on STTCNQ under optimized conditions at concentrations of: (1) 2.0, (2) 4.4, (3) 8.4, (4) 12.5, (5) 17.2, (6) 22.8, (7) 29.2, (8) 36.4, (9) 43.2, (10) 52.2, (11) 61.4, (12) 69.8, (13) 78.8, (14) 86.6, and (15) 100 $\mu\text{mol l}^{-1}$ (a) and calibration plot (b). Applied potential of 0.15 V

case, the value of determined Γ was 4.6 nmol cm^{-2} . The average k_b was $1.07 \times 10^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value was similar or greater than the reported by others researchers using other modifiers, such as nickel hexacyanoferrate and cobalt pentacyanonitrosylferrate [16, 40]. Additionally, the average diffusion coefficient for hydrazine in buffered aqueous solutions (400, 500, 550, and 650 $\mu\text{mol l}^{-1}$) at pH 7.0 calculated from the Koutecky–Levich plot was $5.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is similar to those reported by Abbaspour and Kamyabi [19].

Characteristics of the CPE/STTCNQ

Characteristics of the CPE/STTCNQ were verified by amperometry. In the chronoamperometric measurements, an initial study was performed to determine the best potential to be applied on the electrode (0.070, 0.100,

0.125, 0.150, 0.175, and 190 V vs SCE). The applied potential was chosen based on measurements of the catalytic current in the optimized conditions and the highest current was verified at an applied potential of 0.15 V vs SCE (Fig. 7). Figure 8a shows the amperogram recorded for different concentrations of hydrazine in solution and a linear response resulted from 2 to 100 $\mu\text{mol l}^{-1}$ (Fig. 8b), which can be expressed according to the equation: $j_p/\mu\text{A} = 0.13 (\pm 0.01) + 0.36 (\pm 0.02) [\text{hydrazine}]/\mu\text{mol l}^{-1}$, with a correlation coefficient of 0.999 (for $n=15$). The sensitivity of the proposed method was higher than those reported in literature (Table 1). Such good sensitivity can be attributed to the efficiency of the electron transfer between the modified electrode and hydrazine, favored by a high-reaction rate (k_b) and the low-charge transfer resistance of the CPE/STTCNQ, as a consequence of a highly dispersed LiTCNQ on the ST. The detection and quantification limits were estimated as 0.6 and 2.0 $\mu\text{mol l}^{-1}$, respectively, using $3\sigma/\text{slope}$ and $10\sigma/\text{slope}$ ratio, respectively, where σ is the standard deviation of the mean value for ten voltammograms of the blank, determined according to the IUPAC recommendations [47]. The response time, considering the time to reach 100% of the signal, was approximately 1 s. These amperometry data when compared with those reported in the literature for other modified electrode [9–16, 20, 21, 23, 41–46] showed a better performance to the CPE/STTCNQ.

Stability of CPE/STTCNQ

The stability of the CPE/STTCNQ was checked in presence of hydrazine performing successive chronoamperometric

measurements. After 140 amperometric measurements, no change was observed in the amperometric behavior of the modified electrode. When the modified electrode was stored at room temperature, no significant change in the response was observed for 2 months.

The modified electrode presented a good repeatability for hydrazine determinations. The relative standard deviation (RSD) of the peak current for ten determinations in phosphate buffer (pH 7.0) solutions containing 100 $\mu\text{mol l}^{-1}$ hydrazine was 4.2%. Additionally, a series of ten modified electrodes prepared in the same manner was also tested and the relative standard deviation observed was only 4.5%. These experiments indicate that LiTCNQ adsorbed onto ST matrix has good stability and repeatability, probably associated with the ability of the matrix to fix LiTCNQ molecule by a strong adsorption.

Conclusion

This work demonstrated that ST has great potential to be used as a support for immobilizing LiTCNQ to develop new modified electrodes as well as to investigate the behavior of the hydrazine electrooxidation mechanism. This system is a feasible alternative for the analytical determination of hydrazine in aqueous solutions. The modified electrode exhibited high electrocatalytic activity and shifted the hydrazine oxidation overpotential to value less positive when compared to the oxidation on the CPE/ST. The high stability presented by LiTCNQ immobilized onto the ST matrix made possible the investigation of the kinetic parameters of the reaction between LiTCNQ and hydrazine,

Table 1 Modified electrodes for electrocatalytic detection of hydrazine

Modified electrode	pH	E_p (V)	LOD ($\mu\text{mol l}^{-1}$)	Sensitivity ($\mu\text{A } \mu\text{mol l}^{-1}$)	Reference
Lithium tetracyanoquinodimethanide adsorbed onto a silica gel modified with titanium oxide	7.0	0.15	0.6	0.36	This work
Hydroquinone salophen derivatives modified GCE	7.0	0.2	1.6	~0.02	[10]
Polymeric iron-tetraaminophthalocyanine modified electrode GCE	13.0	-0.2	–	–	[11]
Dinuclear ruthenium phthalocyanine (RuPc) modified GCE	12.0	0	0.03	–	[12]
Cobalt phthalocyanine (CoPc) modified carbon paste electrode	13.0	-0.1	100	0.25	[13]
CoPc/cellulose acetate modified GCE	4.7	0.6	1	0.001	[14]
Iron phthalocyanine complex linked to mercaptopyridine self-assembled monolayer	7.0	0.35	5 and 11	0.016	[15]
Ni-hexacyanoferrate modified carbon ceramic electrode	7.0	0.55	0.28	0.26	[16]
Carbon nanotube modified microelectrode	7.0	0.50	1.0	–	[20]
Pyrogallol red modified GCE	9.0	0.2	1.7	0.08	[21]
Chlorogenic acid/carbon ceramic composite electrode	8.0	0.25	20	0.22	[23]
Pd/CNT/4-aminobenzene monolayer graphed GCE	4.0	0.40	1.0	–	[41]
Pd-modified electrochemical detector for capillary electroforesis system	7.3	0.5	1.5	–	[42]
Pd-modified carbon fiber microdisk array electrode	5.5	0.5	1.0	–	[43]
Cu–Pd alloy nanoparticle modified SPE	7.4	0.2	0.27	0.21	[44]
Nafion/Ru ³⁺ modified GCE	1.0	1.0	0.1	–	[45]
Nafion/lead ruthenium oxide pyrochlore modified GCE (FIA)	7.0	0.7	0.15	0.13	[46]

employing RDE. In comparison with previously published values, can conclude that the measured k_b value is among the highest reported so far. Under optimized conditions, amperometry measurements in phosphate buffer (pH 7.0) solutions yielded lower detection limits and high sensitivity for hydrazine. The modified electrode also showed good repeatability (SD=4.2%) and stability for hydrazine sensing. These results, when compared to others reported in the literature, suggest that the CPE/STTCNQ system can be used as an efficient catalyst for hydrazine oxidation in aqueous solutions.

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