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Electrocatalytic Oxidation of Formaldehyde on Novel Composite of Nickel/triton-x100/poly(o-aminophenol-co-aniline)

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Abstract

Oxidation of formaldehyde (HCHO) is very important, due to its use in fuel cells. Modification of electrodes surfaces is an excellent way to decrease the over potentials while to increase the current density of the voltammetric response.pt as most efficient metal catalyst can easily be poisoned by product of oxidation at a high cost. In this work, an efficient and low cost electrocatalytic system for electrochemical oxidation of formaldehyde in alkaline solution is introduced. For preparation of this modified electrode, copolymeric film on the surface of carbon paste electrodewas formed by successive potential cycling in solution containing o-aminophenol and aniline as monomer and Triton X-100 as a surfactant. Ni(II) ions were incorporated into the electrode surface by immersion of the copolymeric modified electrode in 0.1 M Ni(II) ion solution. The influences of different parameters such as mol ratio of monomers in copolymer formation and the number of potential cycling for copolymer formation on electrocatalytic ability of the modified electrode for formaldehyde oxidation have been investigated and optimized. Results show that modified electrode with copolymeric films, had a higher catalytic effect for formaldehyde oxidation with respect to pure homopolymers (polyaniline or poly(o-aminophenol)). Also addition of Triton -X100 in electropolymerization step, considerably increased catalytic ability of the modified electrode for formaldehyde oxidation. This modified electrode displays a highly efficient electrocatalytic activity

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toward oxidation of formaldehyde. The current density of 11 mA cm^{-2} is greater than most of the previously reported electrodes.

Keywords*:* Electropolymerization, Triton-X100, Electrocatalytic oxidation, Nickel, Formaldehyde.

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Introduction

Over the past few years, one of the most important research fields in electrochemistry has been the control of the structure and reactivity of electrode/solution interfaces through the formation of modified electrodes. The modified electrodes are obtained by incorporating some redox species on the electrode surface, which are capable of producing rapid and reversible changes in their oxidation states. Such species acts as a redox mediator of an electrochemical reaction between the electrode and an electroactive species, present in the electrolyte. Also they can modify the reaction, by lowering its activation energy, decreasing the overpotential and increasing the current intensity, respect to the reaction on the unmodified electrode [1-5].

Development of efficient electrocatalysts for oxidation of small organic molecules such as formaldehyde and methanol has received considerable attention owing to their use in fuel cells.Numerous reports have been published on the electrooxidation of formaldehyde, but most have focused on its electrocatalytic oxidation on nanoparticles (NPs) of noble metals such as Pt and Pd, owing to their superior electrocatalytic properties [6-10]. However, noble metal NPs are expensive. Transition metals such as Ni are attractive alternatives to noble metals in electrocatalytic processes because they are abundant, inexpensive and efficient catalysts. It has been reported that anodic oxidation of transition metals in an alkaline medium forms a metal hydroxide layer, which acts as an efficient catalyst for the oxidation of various substances. In alkaline media, Ni^{2+} species form $Ni(OH)_2$ followed by NiOOH. The NiOOH species can efficiently oxidize various substances such as glucose [11,12], methanol[13,14], ethanol[15,16], and some drugs [17,18]. Numerous reports have been published on the electro oxidation of formaldehyde on Ni-containing electrodes such as Ni/P(NMA)/MCPE [19], Ni/P(1,5-DAN)/MCPE [20], Ni/POT(TX-100)/MCPE [21], nanoporous nickel phosphate modified glassy carbon [22], nickel nano particle/indium tin oxide [23] and nickel-Hydrogen Titanate Nanotubes / carbon paste electrode [24].

Maximovitch and Bronoel [25] reported that it is difficult to measure the oxidation current of methanol on smooth nickel because it is difficult to obtain the surface free from adsorbed oxygen. Smooth nickel is very sensitive to Molecular oxygen dissolved in the solution that adsorbs on the electrode and inhibits the reaction. Dispersion of nickel in a polymeric substrate can solve this problem.It is well known that conducting polymers (CPs) with porous structures and high surface areas have been proved to be suitable host materials for dispersion of metallic particles [26-30]. In the previous works, we used the nickel/poly(o-aminophenol) modified carbon paste electrode, nickel/SDS/poly(o-aminophenol) modified carbon paste electrode and nickel/SDS/poly(n,n dimethylaniline) modified carbon paste electrode for electrocatalytic Oxidation of methanol [31, 32, 33], ethylene glychol [32], carbohydrates [34] and some antibiotic drugs [35]. This study showed that the metal-polymer electrodes are easy to prepare, stable for long-time periods with good detection limits, and have widelinearrangeresponses**.** Moreover, these studies show that presence of SDS as an anionic surfactant in electropolymerization solution, can considerably improve catalytic strength of nickel hydroxide dispersed on resulting polymer.

On the other hand, in the family of conductive polymers, aniline is a molecule used to modify electrode surfaces, forming the polyaniline polymer (PANI). It has received considerable attention for its special properties: it is a conducting polymer with high stability, interesting electrochemical and optical characteristics, low cost and easy preparation [36-38]. The electropolymerization of aniline by continuous potential scanning allows the study of the redox properties of the electrogenerated films and their growth. Additionally, in recent years a wide variety of copolymers have been studied for many different applications[39-48]. Copolymerization can be used as a technique to improve the properties of a material.

Owing to the above-mentioned advantages of the polymer modified electrodes, positive effect of surfactant application and advantages of copolymerization, in this paper we decide to combine all of these techniques for preparation of a new and effective electrocatalytic system. Copolymerization was done by the simultaneous electropolymerization of aniline and o-aminophenol in aqueous H_2SO_4 solution containing non ionic surfactant of Triton -X100 (T-X100), by cyclic voltammetry method. Then nickel ions were incorporated in polymer backbone and resulting electrode was used for electrocatalytic oxidation of formaldehyde in NaOH solution.

Experimental

Reagent and materials

O-aminophenol (Merck) was purified by recrystallization in ethylacetate and dried under vacuum. Sulfuric acid from Fluka was used as the supporting electrolyte. High viscosity paraffin (density: 0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter: 0.10 mm) from Merck was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

Instrumentation

Electrochemical experiments were performed on SAMA500 potentiostat with a voltammetry cell in a three electrode configuration. Ag/AgCl/KCl (3 mol/L) was used as reference electrode; a platinum wire as the auxiliary electrode. Working electrode was a homemade carbon paste electrode which was further modified by electropolymerization.

Preparation of Working Electrode

A mixture of graphite powder and paraffin was blended by hand mixing with a mortar and pestle for preparation of carbon paste. The resulting paste was then inserted in the bottom of a glass tube (internal radius: 1.7 mm). The electrical connection was implemented by a copper wire lead fitted into the glass tube. A fresh electrode surface was generated rapidly by extruding a small plug of the paste with a stainless steel rod and smoothing the resulting surface on white paper until a smooth shiny surface was observed.

Electropolymerization procedure

Poly(aniline) (PANI), poly(o- aminophenol) (POAP) and poly(o- aminophenol -co-aniline) (POAP-co-PANI) films were grown at carbon paste electrode by applying cyclic potential sweeps (100 mVs^{-1}). The polymerization of aniline or OAP was carried out in 10 mM monomer, 0.5 M H_2SO_4 + 20 mM T-X100 aqueous solutions. In the case of copolymers, the total monomers concentrations were 10 mM with different mole fractions from OAP and ANI.

Incorporation of Ni(II) ions into a polymeric matrix

In order to incorporate Ni(II) ions into the homopolymeric and copolymeric film, the freshly electropolymerized electrode was placed at an open circuit well stirred aqueous solution of 0.1 M nickel nitrate. The accumulation of nickel was conducted by complex formation between Ni(II) and amine sites in the polymer backbone for a given period of time (t_a, accumulation time).

Results and discussion

Effect of triton x-100 on electropolymerization of aniline and o-aminophenol

Figures 1 and 2 show electropolymerization of ANI and OAP in the absence and presence ofT-X100 as a non ionic surfactant. Comparison of these voltammograms shows that addition of a T-X100 to electropolymerization solution effectively increased the peak current of monomer oxidation (in the first cycle) and electropolymerization rate of both monomers. Similar to such effect was previously reported with us about another surfactant, sodium dodecyl sulfate (SDS), on electropolymerization rate of the poly (o-aminophenol) [32] and poly (n, n dimethylaniline) [33].

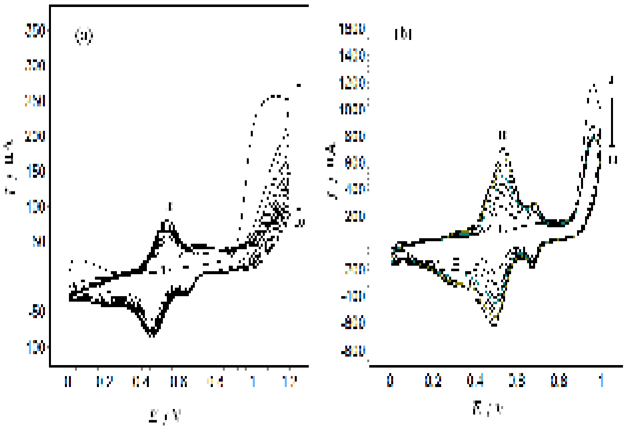

Figure 1. Electropolymerization of aniline in the solution of 10 mM ANI monomer/0.5M H_2SO_4 at the surface of carbon paste electrode (a) in the absence and (b) in presence of 20 mM T-X100 at scan rate of 100 mV s^{-1}. The arrows indicate the trends of current during CVs.

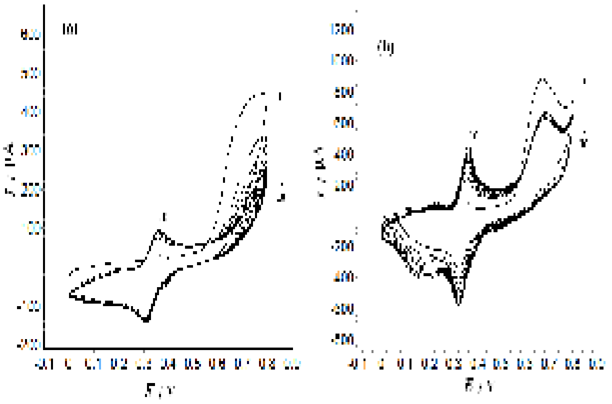

Figure 2. Electropolymerization of o-aminophenol in the solution of 10 mM OAP monomer/0.5 M H_2SO_4 at the surface of carbon paste electrode (a) in the absence and (b) in presence of 20 mM T-X100 at scan rate of 100 mV s^{-1}. The arrows indicate the trends of current during CVs.

Effect of monomer ratio

The characteristics of electrochemical copolymerization are highly dependent on the synthesis conditions, in particular, the mole fraction of each of the monomers involved in the reaction [42, 46, 47, 48].

In order to find the best ratio of monomers in copolymerization, different copolymers were prepared using solution containing different percentages of two monomers. Then nickel ions were incorporated in copolymers backbone. Resulting electrodes were used for electrocatalytic oxidation of formaldehyde in NaOH solution. Results show that copolymer prepared with 10 % o-aminophenol and 90% aniline solution has highest electrocatalytic current for formaldehyde oxidation (figure 3). Therefore, this ratio of monomers was selected as best ratio for other studies.

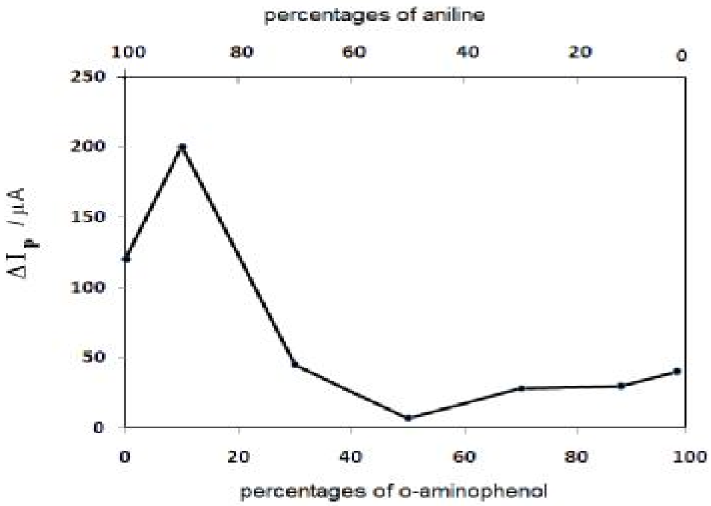

Figure 3. Effect of different percentages of aniline and o-aminophenol, in electropolymerization solution, on catalytic ability of the modified electrode for oxidation of formaldehyde.

Effect of polymer thickness

Ability for control of polymer thickness is one of the advantages of electropolymerization, which in cyclic voltammetry can do by controlling the number of potential cycles. Figure 4 shows dependence of electrocatalytic currentfor formaldehyde oxidation respect to number of cycles of electropolymerization.

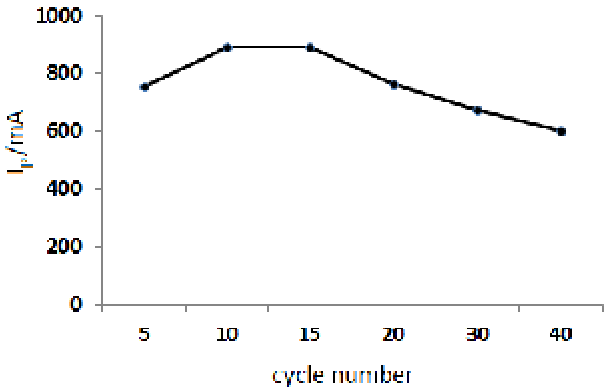

Figure 4. Effect of different Cycle numbers, in potentiodynamic formation of copolymer, on catalytic ability of the modified electrode for oxidation of formaldehyde.

As can be seen the copolymer prepared with 10 and 15 cycles has higher electrocatalytic currentfor formaldehyde oxidation and after 15 cycles, the current will be decreased, which probably is due to decreasing of polymer conductivity with increasing of its thickness. Therefore, the number of 10 cycles (which needs shorter time) was selected for other studies.

Electrocatalytic oxidation of formaldehyde on the modified electrodecyclic voltammetry studies

The electrochemical response of Ni/T-X100/(POAP-co-PANI)/CPE in alkaline solution (i.e., 0.1 M NaOH) exhibits well defined anodic and cathodic peaks (Figure 5a), which was related to the oxidation of $Ni(OH)_2$ to NiOOH and reduction of NiOOH to $Ni(OH)_2$. The surface coverage of the immobilized active substance (Ni(II)) in the films can be evaluated from the charge under the current–potential wave with correction for the baseline ($\Gamma^* = Q/nFA$). The value of Γ^* for Ni/T-X100/(POAP-co-PANI)/CPE was 2.17×10^{-7} mol cm^{-2}. As can be seen in Figure 5b, upon formaldehyde addition (100 mM) there is an increase in the anodic peak current and a decrease in the cathodic peak current. This behavior is typical of that expected for the mediated oxidation (EC' mechanism) as follows:

$$Ni(OH)_2 + OH^- \longleftrightarrow NiOOH + H_2O + e^- \qquad E$$

$$NiOOH + \text{formaldehyde} \longrightarrow Ni(OH)_2 + \text{Product} \qquad C'$$

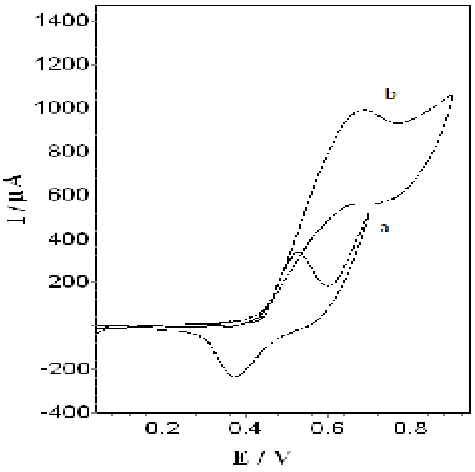

Figure 5. Cyclic voltammograms of Ni/T-X100/(POAP-co-PANI)/CPE, a) in the absence and b) in presence of 0.1 M formaldehyde in 0.1 M NaOH solution at scan rate of 10 mV s^{-1}.

Electrocatalytic oxidation of formaldehyde on the surface of different electrodes was shown in Figure 6. Comparison of Figure 6a and Figure 6d show that addition of T-X100 in electropolymerization step considerably increased catalytic ability of the modified electrode. Also comparison of Figures6d, 6b and 6c show that copolymer modified electrode has higher catalytic ability respect to homopolymer modified electrodes.

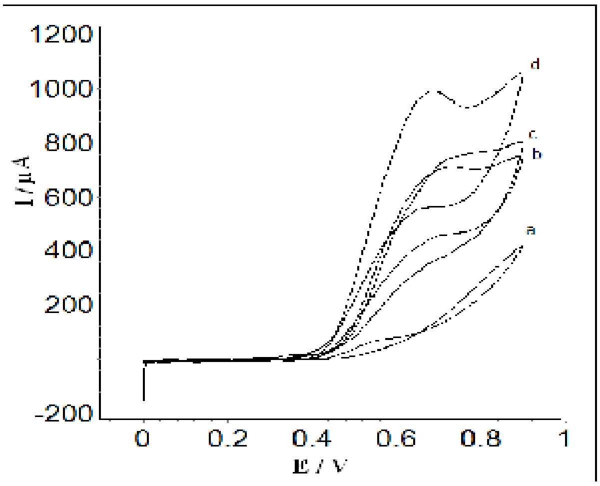

Figure 6. Cyclic voltammograms of a) Ni/(POAP-co-PANI)/CPE, b)Ni/T-X100/(POAP)/CPE, c) Ni/T-X100/(PANI)/CPE and d) Ni/T-X100/(POAP-co-PANI)/CPE in presence of 0.1 M formaldehyde at scan rate of 10 mVs^{-1}.

Figure 7 shows the effect of formaldehyde concentration on the anodic peak current at Ni/T-X100/(POAP-co-PANI)/CPEin 0.1 M NaOH. It is clearly observed that as the formaldehyde concentration increases, the peak height increases linearly with formaldehyde concentration up to 100 mM. It can be assumed that the increase is due to the presence of a diffusion controlled process that appears to play an important role at low formaldehyde concentrations. While the formaldehyde concentration exceeds this limit, the rate of the whole oxidation process seems to be limited by that of the catalytic process in origin and its rate depends on the reaction between formaldehyde and Ni(III) species, which is present in the film.

Chronoamperometric studies

Double potential step chronoamperometry is employed for the investigation of electrochemical processes at the Ni/T-X100/ (POAP-co-PANI)/CPE surface. Fig. 8A shows the double step chronoamperograms for the modified electrode by setting the working electrode potential at 0.650 V (first potential step) and 0.350 V (second potential step) vs. Ag|AgCl|KCl (3 M) for various concentrations of formaldehyde.

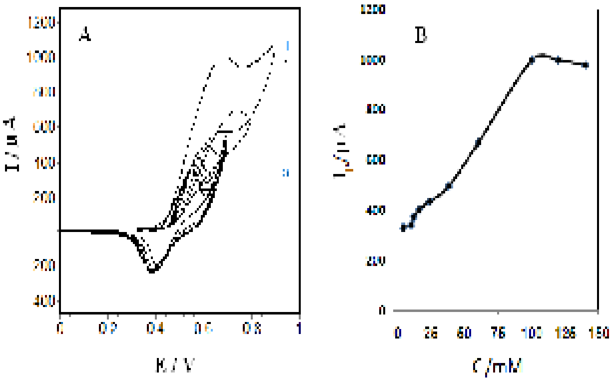

Figure 7. A) Current–potential curves of different formaldehyde concentrations: (a) 0.0 M, (b) 0.004 M, (c) 0.01 M, (d) 0.012 M, (e) 0.016 M(f), 0.024 M, (g) 0.038 M, (h) 0.06 M and (i) 0.1 M at the surface of Ni/T-X100/ (POAP-co-PANI)/CPE at the potential scan rate of 0.01 Vs-1. B) plot of Ip vs. formaldehyde concentration.

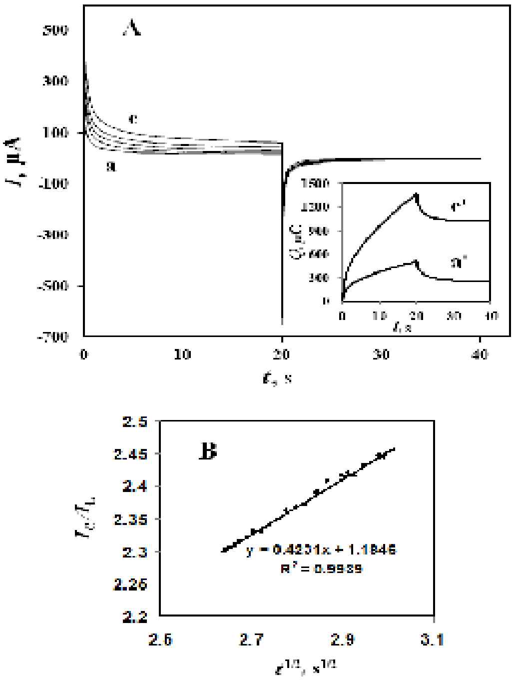

Figure 8. A) Chronoamperograms obtained at the Ni/T-X100/ (POAP-co-PANI)/CPEin the absence (a) and presence of b) 10, c) 15, d) 20 and e) 30 mM of formaldehyde in 0.1 mol L^{-1}NaOH solution, first and second potential steps were 0.65 and 0.35 V (inset). Dependence of Q (µC) vs. t, (a') and (e') respectively derived from the data of chronoamperograms (a) and (e) B). Dependence of I_C/I_L on $t^{1/2}$ derived from the data of chronoamperogams of (a) and (e).

In the presence of formaldehyde, the charge value associated with the forward chronoamperometry, Q_a, is greater than that observed for the backward chronoamperometry (Inset of Fig.8 (e')). Chronoamperometry can also be used for the evaluation of the chemical reaction between the formaldehyde and modified layer (catalytic rate constant, k) according to [49];

$$I_C/I_L = \gamma^{1/2}\pi^{1/2} = \pi^{1/2} (kc_o t)^{1/2}$$

Where I_C and I_L are the currents in the presence and absence of formaldehyde, k is catalytic rate constant; c_o is the bulk concentration of formaldehyde and t is the elapsed time.From the slope of the I_C/I_L vs. $t^{1/2}$ plot, presented in Fig. 8B, the mean value of k for the concentration range of 10 – 30 mM of formaldehyde is obtained as 1.90×10^3 $cm^3 mol^{-1} s^{-1}$.

Performance of the proposed electrode was investigated by a comparison between Ni/T-X100/ (POAP-co-PANI)/CPE and some of the previously reported modified electrodes. Table 1 show that Ni/T-X100/(POAP-co-PANI)/CPE displays a highly efficient electrocatalytic activity toward oxidation of formaldehyde. As seen from the Table, the current density of 11 mA cm^{-2} is comparable with amount reported for higher potential scan rate by Raoof et.al [21], and is greater than most of the previously reported electrodes, containing polymeric modified electrodes [19, 20], platinum modified electrodes [50,51] and some nanoparticle modified electrodes [22-24]. Also, this electrode has some advantages, such as low cost, ease of preparation and very low residual current.

Table 1. Comparison of the efficiency (in terms of current density) of some modified electrodes used in electrocatalytic oxidation of formaldehyde.

Electrode	j^a ($mAcm^{-2}$)	V ($mV\ s^{-1}$)	C(HCHO) (M)	Ref
Ni/P(NMA)/MCPE	4.1	20	0.07	19
Ni/P(1,5-DAN)/MCPE	0.76	10	0.17	20
Ni(OH)2/POT(TX-100)/MCNTPE	12.1	20	0.048	21
Pt/C	10.26	50	0.5	50
Pt/Pt	10.3	30	0.75	51
Nano-NiPh/GC	10	50	0.005	22
NiNPs/ITO	2.5	100	0.16	23
Ni-HTN/CPE	4.5	25	0.13	34
Ni/T-X100/(P*o*AP-co-PANI)/CPE	11	10	0.1	This work

[a] current density: I_{pa} / A (A is the geometric surface area of substrate.
Ni/P(NMA)/MCPE: nickel/poly(N-methylaniline)/modified carbon paste electrode
Ni/P(1,5-DAN)/MCPE: nickel/poly (1,5 diaminonaphthalene)/modified carbon paste electrode
Ni(OH)2/POT(TX-100)/MCNTPE: nickel hydroxide/poly(o-toluidine)/triton x-100 /modified carbon nanotube paste electrode
Nano-NiPh/GC: nanoporous nickel phosphate modified glassy carbon
NiNPs/ITO: nickel nano particle/indium tin oxide
Ni-HTN/CPE:nickel- Hydrogen Titanate Nanotubes/ carbon paste electrode

Conclusion

In this study, we have used Ni/T-X100/ (POAP-co-PANI)/CPE for electrocatalytic oxidation of formaldehyde.Results showed that utilization of TX-100 as an additive during the electropolymerization process enhanced the electrocatalytic activity of the modified electrode towards formaldehyde oxidation. Also modified electrode with copolymeric films show higher catalytic effect for formaldehyde oxidation respect to pure homopolymers (polyaniline or poly(o-aminophenol)).

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