

Electro-Catalytic Oxidation of Methanol at Ni(OH)₂ Nanoparticles-Poly (o-Anisidine)/Triton X-100 Film onto Phosphotungstic Acid-Modified Carbon Paste Electrode

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ABSTRACT: In this work, Phosphotungstic Acid modified Carbon Paste Electrode (PWA-CPE) is used as a substrate for electro-polymerization of o-Anisidine (OA). Also, Triton X-100 (TX-100) surfactant is used as an additive for electrochemical polymerization of OA onto the PWA-CPE, which is investigated as a novel matrix for dispersion of nickel species. The prepared electrodes are characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and electrochemical methods. Growth of the poly o-Anisidine (POA) film in the absence of TX-100 and/or PWA is very poor, while it considerably increases in the presence of them. The methanol oxidation and stability of the Ni/POA (TX-100)/PWA-CPE are investigated by various electrochemical techniques. It has been shown that the poly (o-Anisidine)/Triton X-100 (POA (TX-100)) at the surface of PWA-CPE improves the catalytic efficiency of the dispersed Ni(OH)₂ nanoparticles towards methanol oxidation.

KEYWORDS: Electro-catalysis; Methanol; Ni(OH)₂ nanoparticles; Poly (o-Anisidine)/Triton X-100 film; Phosphotungstic acid.

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INTRODUCTION

There is considerable attention in the electro-oxidation of methanol because of the development of Direct Methanol Fuel Cells (DMFCs) as power sources for electric vehicles and electronic devices. The success of the DMFC mainly depends on the design and ground work of high recital anode catalysts. To supplement efficiency of the DMFC, an active and low fee catalyst should be developed. Pt-based catalysts are recognized as the best catalysts for low temperature fuel cells [1]. However, the limited use of Pt-based electro-catalysts comes from their high cost and limited supply of Pt [2]. Nickel based anodes have less poisoning effect than Pt-based electrodes for methanol oxidation in alkaline media and also are inexpensive [3, 4]. On the other hand, one tactic to advance the stability of the catalyst is to disperse the catalyst particles on the conductive support due to its porous structures to reduce the catalyst loading by keeping high catalytic activity [5, 6].

The heteropolyacids (HPAs) are super ionic proton conductors in their fully hydrated states [7, 8]. Among the Keggin-type HPAs, phosphotungstic acid ($H_3PW_{12}O_{40}$, PWA) is the strongest Bronsted super acid and has the highest conductivity. PWA possesses a unique distinct ionic structure and exhibits extremely high proton conductivity [9]. $H_3PW_{12}O_{40}$ with Keggin-type structure consisted of one PO_4 tetrahedron surrounded by four W_3O_{13} sets formed by three edge-sharing octahedral. There were four kinds of oxygen atoms in $H_3PW_{12}O_{40}$. It is well known that HPAs such as PWA are widely used as an additive for proton exchange membranes [10, 11].

Conducting Polymers (CPs) with high surface area, environmental stability and porous structures improve the properties of the electrode-electrolyte interface and allow a facile flow of electronic charges during the methanol oxidation on the catalyst particles [12-14]. The greatest of the known CPs is anion-doped in their conducting forms. Reversible doping-undoping processes of the CPs depend on the solution acidity, the presence of appropriate anions in solution, and the polymer structure [15]. When the polymers were doped with the polyanions, especially in the course of their preparation, many CPs cannot expel them into the solution and can be irreversibly incorporated into polymer, yielding new composite materials. *Sung et al.* [16] studied the electrochemical properties of polypyrrole (Ppy) containing heteropolytungstate anions. *Fabre et al.* [17]

incorporated an iron-substituted heteropolytungstate anion into different CPs, and showed that this anion can be efficiently retained in poly (*N*-methylpyrrole) films. Three dodecaheteropolyacids were entrapped into polyaniline (PANI) and Ppy: $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, and $H_4SiW_{12}O_{40}$, yielding a composite catalyst for conversion of ethanol into ethylene, diethyl ether, and acetaldehyde [18]. PANI and some aromatic poly (azomethines) were doped with heteropolyacids $H_3PW_{12}O_{40}$ and showed to catalyze the conversion of isopropanol [19].

The diversity of results for the conductivity of the Poly *o*-Anisidine (POA) film reported in the literature [20-22] shows that the electrochemical response of POA is strongly influenced by the experimental procedure, dopant anions and the purity starting monomer. On the other hand, surfactants play asignificant role in the electrode reactions by providing specific orientation of the molecules at the electrode interface. Surfactants affect the locus of polymerization and thus modify the surface morphology of polymers. Micellar media affect the electrochemical reactions by irreversible adsorption, leading to a change in the solution-electrode interface properties and producing some template effects at the electrode [23]. Moreover, media containing surfactant can also stabilize charged species such as anions or cation-radicals [24-26]. The effect of Triton X-100 (TX-100) on the electro-polymerization of CPs in aqueous solutions has been investigated [27-30]. The CPs films formed in the presence of TX-100 had improved properties than those obtained with other conditions. Generally, studies involving use of the surfactant in electro-preparation of novel CPs supports is occasional.

In present work, a simple, novel and timesaving procedure has been developed for the electro-oxidation of methanol. An evaluation of literature has given no evidence about the utilization of the PWA and TX-100 for the electro-polymerization of OA. Therefore, POA/TX-100 modified PWA-CPE as a new conductive matrix was prepared and allowed an improved dispersion of nickel species as a low cost catalyst for methanol oxidation.

EXPERIMENTAL SECTION

Materials

H_2SO_4 (98%, Merck) and NaOH (98%, Merck) were used for the preparation of supporting electrolytes. $NiSO_4 \cdot 6H_2O$ (99%, Merck) and CH_3OH (>98%, Merck),

OA (99%, Merck) were used as received. K₃Fe(CN)₆, K₄Fe(CN)₆ (>99%, Merck) and KCl (>99%, Merck) were used for electrochemical impedance studies. The solvent for the preparation of the reagents solutions was double distilled water. High viscosity paraffin (density: 0.86 g/cm³, Fluka) was used as the pasting liquid for PWA-CPE. Graphite powder (particle diameter: 0.10 mm, Merck) and PWA were used as the working electrode substrates.

Instrumentation

The surface morphology of the sample was examined by using Scanning Electron Microscopy (SEM, Philips XL 30) and Energy Dispersive Spectrometer (EDS) was used to identify the sample elemental composition. Electrochemical experiments and Electrochemical Impedance Spectroscopy (EIS) were performed on potentiostat/galvanostat Autolab (GPES software model PGSTAT 302N, Metrohm, Netherlands) coupled with a Metrohm voltammetry cell in a three electrode configuration at room temperature. Ag|AgCl|KCl (3 M), Pt wire and PWA-CPE were used as a reference, auxiliary and working electrodes, respectively.

Preparation of the modified electrode

The PWA-CPE was prepared by mixing PWA, graphite powder and paraffin oil with a 10:60:30% (W/W) ratio. The CPE was prepared by hand-mixing the graphite powder and paraffin oil with a 70:30% (W/W) ratio to be used for comparison purposes. The paste was carefully mixed and homogenized in an agate mortar for 20 min. The paste was packed firmly into a cavity (3.9 mm in diameter, geometric surface area of 0.12 cm²) at the terminal of Teflon tube. Electrical contact was established through a copper wire which was connected to the paste in the inner hole of the tube. The electrode surface was mildly smoothed by rubbing on a piece of a weighing paper prior to use. This procedure was also used to renew the surface of PWA-CPE. A later modification of the mentioned electrodes was performed in three steps:

(a) Electrochemical polymerization of OA by using potential cycling (10 cycles at $v = 50$ mV/s) in a solution containing 5.0 mM OA, 0.5 M H₂SO₄ and 5.0 mM of TX-100 for construction of POA (TX-100)/PWA-CPE.

(b) Accumulation of Ni²⁺ ions by immersion the freshly electro-polymerized POA (TX-100) in a well-stirred aqueous 0.1 M NiSO₄ solution for 2 min. The Ni²⁺ ions link covalently to the amine groups in the POA (TX-100) backbone creating a stable structure [27, 31].

(c) Immersing the Ni/POA (TX-100)/PWA-CPE in 0.1 M NaOH solution and potential cycling between 0.1 to 0.8 V vs. Ag|AgCl|KCl (3 M) at $v = 50$ mV/s. This electrode was studied after reaching constant electrochemical behavior. The geometric surface area of the electrode was used to analyze the current density of methanol oxidation. All experiments were conducted at ambient temperature. Table 1 summarizes the several surface parameters including polymer mass, film thickness, surface coverage of nickel, anodic electron transfer coefficient and electron transfer rate constant for the Ni/POA (TX-100)/PWA-CPE.

RESULTS AND DISCUSSION

Electrochemical polymerization

In this work, electro-polymerization of OA was investigated on both of bare CPE and PWA-CPE. The successive Cyclic Voltammograms (CVs) which were recorded during the electro-polymerization on the CPE were presented in Fig. 1A. As can be seen in this figure, it is understandable that at the first cycle in the positive scan, OA oxidation to its radical cation takes place. By continuous potential cycling, the peak shifts to more positive directions and its altitude decreases. The polymer peaks don't increase significantly with potential cycling. This can express this fact that soluble products adsorb and/or react on surface and do not allow OA to spread the electrode surface to produce more cation-radicals. Fig. 1B shows the polymerization pattern of the OA on PWA-CPE, which has an oxidation peak at about 0.80 V vs. Ag|AgCl|KCl (3 M) at 1st cycle. The peak potential of the OA oxidation shifts from 0.84 V at the CPE to 0.80 V vs. Ag|AgCl|KCl (3 M) on the PWA-CPE. Also, it should be noted that the lower onset oxidation potential of monomer was detected at the PWA-CPE indicating the facile oxidation. As cyclic voltammetry continues, the peak current densities related to the oxidation-reduction of the polymer are slowly increased. This result may be due to specific interactions between radical-cations which are formed during the 1st step of electro-polymerization, and high conductivity in the surface. This is due to that

Table 1: Surface parameters of the Ni/POA (TX-100)/PWA-CPE.

Surface parameter	Value
Polymer mass, $W_{POA}/\mu\text{g}$ ($\eta Q_{\text{dep}}M/Fn$)	10.4
Polymer thickness, $d_p/\mu\text{m}$ ($\eta Q_{\text{dep}}M/\rho A_gFn$)	0.55
Ni loading, $W_{Ni}/\text{mg cm}^{-2}$	9.33×10^{-4}
Surface coverage, $\Gamma_{\text{Polymer}}/\text{mol cm}^{-2}$ ($4RTI_p/n^2F^2vA_g$)	4.11×10^{-5}
Surface coverage, $\Gamma_{Ni}/\text{mol cm}^{-2}$	1.59×10^{-8}
*Anodic electron transfer coefficient, α	0.65
**Apparent charge transfer rate constant, k_s/s^{-1}	0.071

$$^*E_{pa} = E^0 + A \ln [(1-\alpha)/m], \quad E_{pc} = E^0 + B \ln [a/m], \quad A=RT/(1-\alpha)nF, \quad B=RT/\alpha nF, \quad m=(RT/F)(k_s/nv)$$

$$^{**}\log k_s = a \log (1-\alpha) + (1-\alpha) \log a - \log (RT/nFv) - [\alpha (1-\alpha) nF\Delta E_p]/2.3RT$$

PWA with high conductivity at the electrode surface facilitates the electron exchange between the electrode and OA, so it can increase the polymer growth rate.

Fig. 1C and D show the multi-sweep CVs during electro-polymerization of OA in the presence of 5.0 mM TX-100 on bare CPE and PWA-CPE, respectively. By adding TX-100 to OA solution, the onset oxidation potential of the monomer was shifted to more negative value and rate of the polymerization was increased considerably. In the presence of TX-100, rate of polymerization was noticeably increased and under consecutive potential cycling, peak currents related to the polymer were meaningfully increased. Indeed, the presence of TX-100 decreases the monomer oxidation potential and induces its polymerization.

Fig. 2 presents the redox behavior of some modified CPEs in 0.5 M H_2SO_4 solution. Anodic peaks I and II can be attributed to POA oxidation in leucoemeraldine to emeraldine oxidation states and subsequent oxidation which corresponds to oxidation of head-to-tail dimer, respectively. The anodic peak III is associated with structural conversion from emeraldine to pernigraniline [32]. The POA(TX-100)/PWA-CPE (d) showed a considerable higher peak current density than that others. The electrochemical signals of the conducting POA films which were prepared from solution with TX-100 at PWA-CPE were significantly improved in comparison with CPE. Moreover, their polymers show a better faithfulness than those obtained in the absence of TX-100. The difference in redox currents reflects the surface areas which are accessible to the electrolyte solution. The increase in surface area advances the doping-undoping

rate, which is benefit to ion diffusion and migration [33]. Seemingly, the porous POA (TX-100) film has higher effective surface area, which is needed for supporting the electro-catalyst. The peak to peak potential separation, ($\Delta E_p = 30$ mV) for the main redox peak is close to $59/n$ mV at 25 °C, which identifies that the number of involved electrons is 2 ($n \approx 1.97$). The ratio of anodic to cathodic peak current density (j_{pa}/j_{pc}) is nearly equal to unity.

Electrochemical behavior of the Ni/POA (TX-100)/PWA-CPE

The redox presentation of the polymer films is powerfully dependent on pH of the electrolyte solution. The obtained polymer displays a well-defined redox behavior in an acidic supporting electrolyte solution. The obtained response in 0.1 M NaOH solution shows a total loss of electrode activity (Fig. 3A). However, the film was not tainted under this condition and its response was recovered when the electrode was engrossed in 0.5 M H_2SO_4 solution. The electrochemical response of the modified electrodes in 0.1 M NaOH solution displays well-defined anodic and cathodic peaks which are related to oxidation/reduction of Ni(III)/Ni(II) couple. The noteworthy difference between the cyclic voltammetric behavior of the Ni/POA(TX-100)/PWA-CPE with extra electrodes, is arisen from area under the curve of Ni/POA(TX-100)/PWA-CPE. This upgrading may be resulted by a contact between the Ni^{2+} and TX-100, which are presented in the POA films or Ni^{2+} and PWA with negative charges. This porous structure yields greater available area and, in the situation of introducing nickel with an improved dispersion and/or distribution.

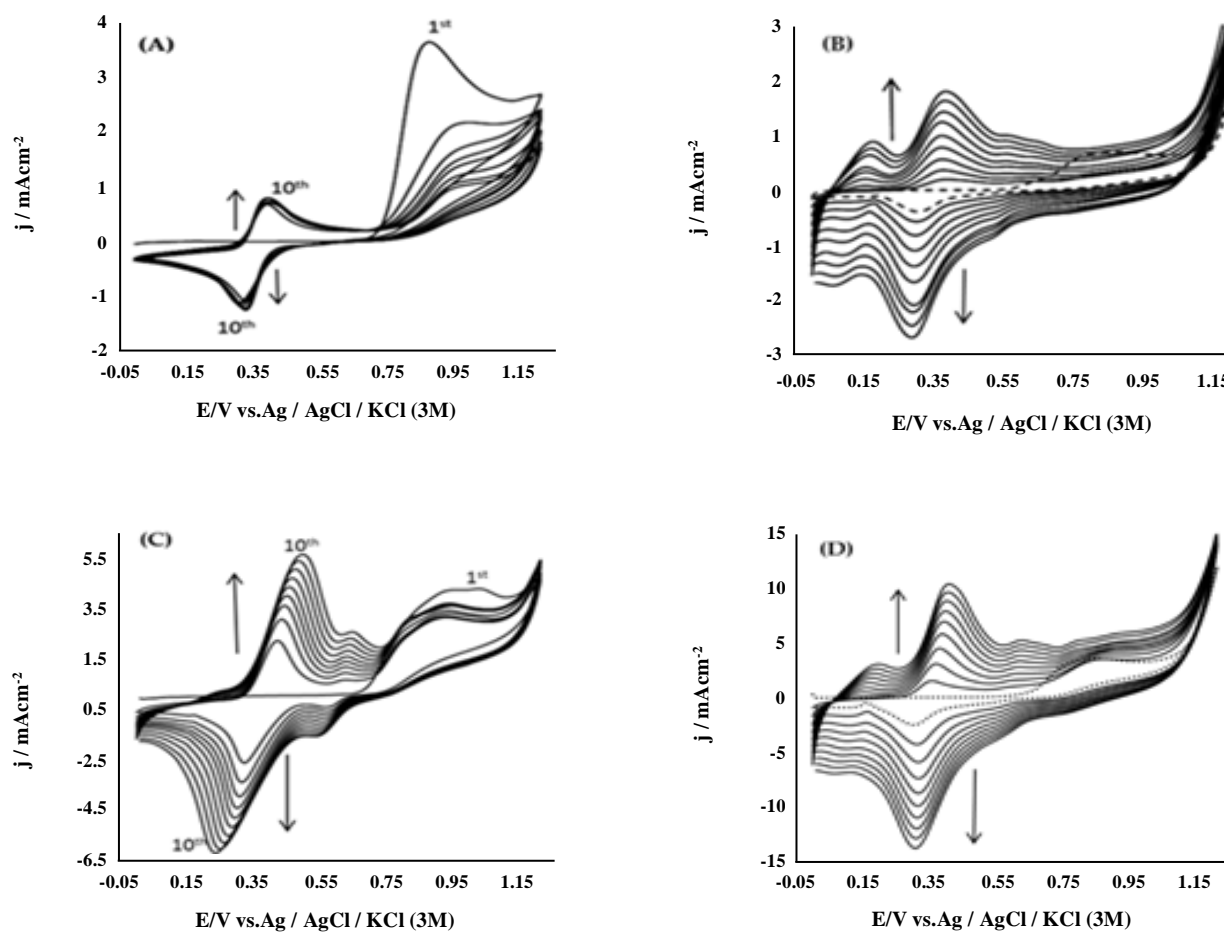


Fig. 1: Potentiodynamic polymerization pattern of 5.0 mM OA in 0.5 M H₂SO₄ solution at (A) bare CPE and (B) PWA-CPE. (C) A+5.0 mM TX-100 and (D) B + 5.0 mM TX-100 at $v = 50 \text{ mV/s}$.

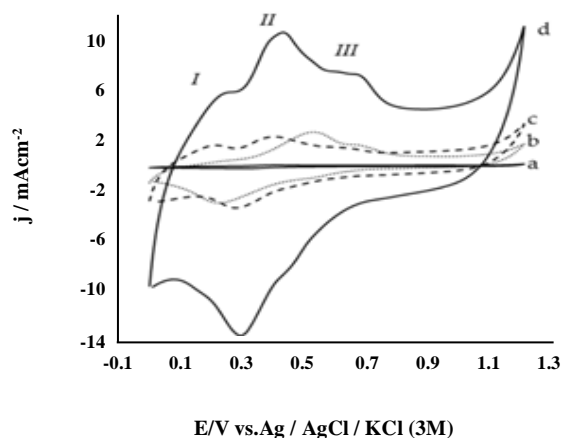


Fig. 2: CVs of the POA/CPE (a), POA/PWA-CPE (b), POA(TX-100)/CPE (c) and POA(TX-100)/PWA-CPE (d) after potential cycling in 0.5 M H₂SO₄ solution at $v = 50 \text{ mV/s}$.

EIS studies

EIS is an operative tool for studying the interface properties of polymer-modified electrodes. The characteristic impedance spectrum (presented in the form of Nyquist plot) comprises a semicircle slice at higher frequencies corresponding to a limited electron-transfer process and a linear part at lower frequency range, representing the diffusion-limited process. The semicircle diameter in the impedance spectrum equals to electron-transfer resistance (R_{et}). This resistance controls the electron-transfer kinetics of the redox probe at the electrode-electrolyte interface. Therefore, R_{et} can be used to designate the interface properties of the electrode-electrolyte. The Nyquist plots of (a) CPE, (b) POA/CPE, (c) POA(TX-100)/CPE, (d) PWA-CPE (trace A) and (a) POA/PWA-CPE, (b) POA(TX-100)/PWA-CPE, (c) Ni/POA(TX-100)/PWA-CPE (trace B) in the presence of

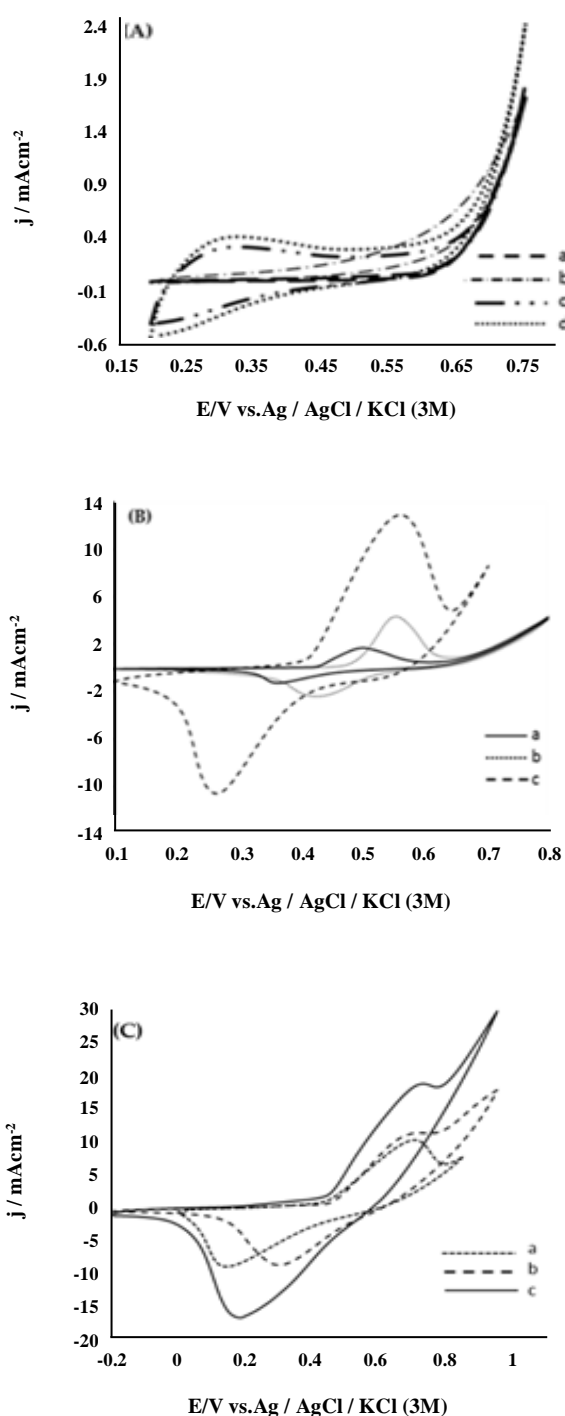


Fig. 3: CVs in 0.1 M NaOH solution at $v = 50 \text{ mV/s}$ of (A); bare CPE (a), PWA-CPE (b), POA (TX-100)/CPE (c) and POA (TX-100)/PWA-CPE (d) (B); Ni/CPE (a), Ni/POA (TX-100)/CPE (b) and Ni/POA/CPE (c) and (C) CVs of Ni/PWA-CPE (a), Ni/POA/PWA-CPE (b) and Ni/POA (TX-100)/PWA-CPE (c).

1.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1) + 0.1 M KCl solution were revealed in Fig. 4. As shown in this figure, the value of R_{et} ($= 50 \Omega$) for POA (TX-100)/PWA-CPE is much smaller than that POA/PWA-CPE ($R_{\text{et}} = 97 \Omega$) and POA (TX-100)/CPE ($R_{\text{et}} = 120 \Omega$) indicating a faster electron-transfer process on the polymeric modified electrode. This may be attributed to the higher real surface area and/or positively charged polymeric skeletons immobilized on the electrode surface which shows a desirability force to $\text{Fe}(\text{CN})_6^{3-/4-}$ ions. On the other hand, $R_{\text{et}} = 23 \Omega$ on the Ni/POA (TX-100)/PWA-CPE shows a minimum value among the other electrodes due to the attendance of nickel species.

Surface morphology

In order to surface characterization, micrographs of the PWA-CPE (a), POA/PWA-CPE (b), POA(TX-100)/PWA-CPE (c) and Ni/POA(TX-100)/PWA-CPE (d) have been investigated by SEM (Fig. 5). The POA on the PWA-CPE surface (trace b) is isolated from each other and its morphology is compact and offers fewer surface defects than that deposited in the presence of TX-100. Electro-polymerization in the presence of TX-100 leads to form a homogenous POA film and relatively uniform coverage (trace c). In this case, more polymers effectively are distributed on the electrode surface, indicating a larger and rougher area which is related to the regular POA film. These results are designing that the surface morphology of the POA film is pointedly influenced by the presence of TX-100. The structure provides a larger available surface area for dispersion and/or distribution of Ni. The average size of $\text{Ni}(\text{OH})_2$ nanoparticles of about 50 nm was obtained (Fig. 5d). Fig. 5e shows the EDS test for elemental analysis of Ni/POA(TX-100)/PWA-CPE. The EDS gives indications for the presence of Ni 3.93 wt% in the nanocomposite. W is originated from PWA which is used as incorporated material into the CPE. The specimens were covered with an ultra-thin coating of gold.

Electro-catalytic oxidation of methanol

Fig. 6A (b) shows the electrochemical behavior of Ni/POA (TX-100)/PWA-CPE in the presence of 0.24 M methanol. The modifier layer $\text{Ni}(\text{OH})_2$ on the electrode surface acts as a catalyst for the oxidation of methanol in 0.1 M NaOH solution. As has been reported in the literature [31,34-38], this behavior is characteristic which is expected in mediated oxidation of methanol. For contrast,

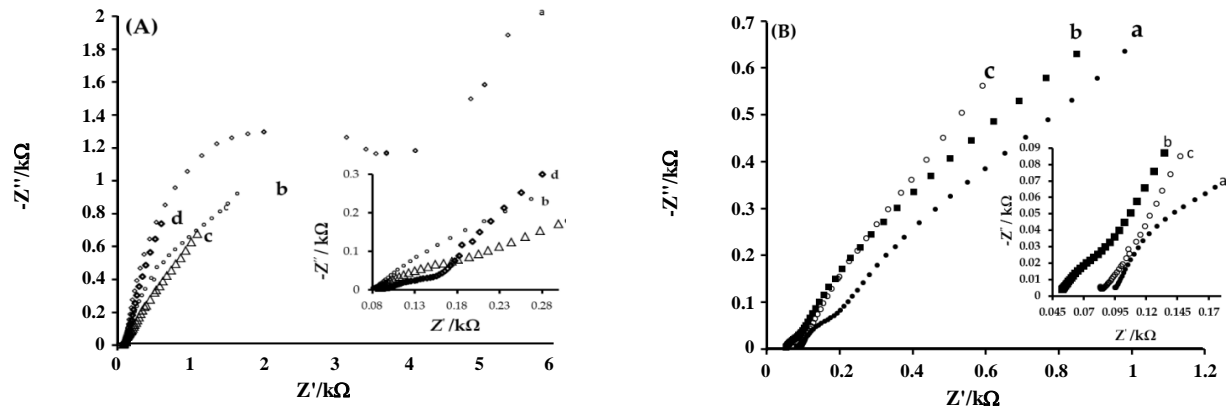


Fig. 4: Nyquist plots of the 1.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ + 0.1 M KCl solution at open circuit potential performed on (A); (a) Bare CPE, (b) POA/CPE, (c) POA (TX-100)/CPE, (d) PWA-CPE and (B); (a) POA/PWA-CPE, (b) POA (TX-100)/PWA-CPE, (c) Ni/POA (TX-100)/PWA-CPE.

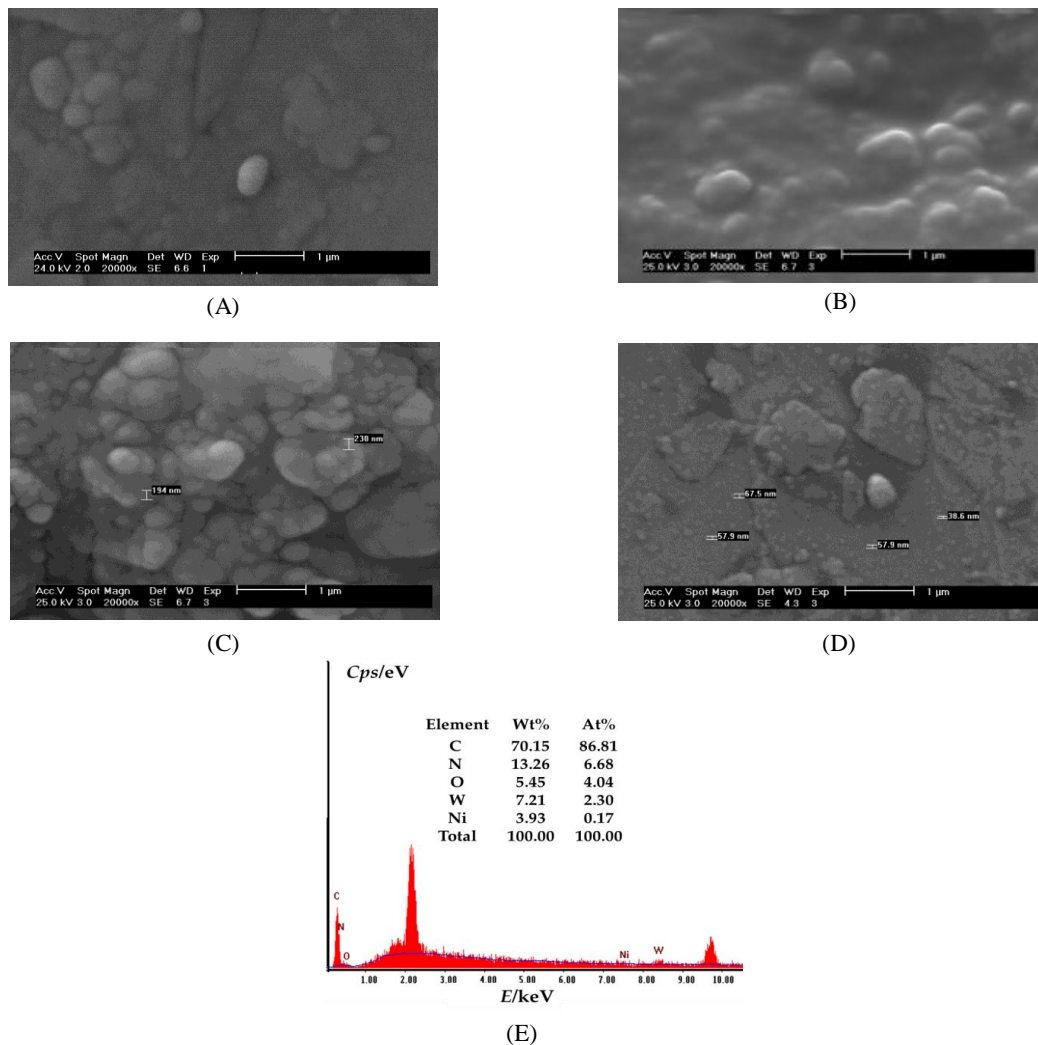


Fig. 5: SEM images of (A) PWA-CPE, (B) POA/PWA-CPE, (C) POA (TX-100)/PWA-CPE, (D) Ni/POA(TX-100)/PWA-CPE, (E) EDS Spectrum of Ni/POA(TX-100)/PWA-CPE.

Table 2: Comparison of the modified electrode with some Ni-modified electrodes used in electro-catalytic oxidation of methanol.

Electrode	Modifier	$a^2j/\text{mA cm}^{-2}$	v/mVs^{-1}	$k/\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	E_p/V	$E_p/\text{V vs. RHE}$	Ref.
CNTPE	Ni/POT (TX-100)	18.5	20	7.40×10^4	0.70	1.66	[27]
CPE	Ni/P-1,5-DAN	1.54	10	-	0.65	1.62	[31]
CPE	Ni/POA	3.7	20	8.67×10^1	0.70	1.66	[34]
GCE	Poly (Ni ^{II} -tmdbt)	1.5	100	-	0.61	1.57	[35]
GCE	Ni(OH) ₂	15.4	50	-	0.58	1.59	[36]
Ni	NiODMG	16.1	20	-	0.62	1.63	[37]
GCE	Poly-Ni(II)-Curcumin	17.2	100	2.04×10^3	0.77	1.78	[38]
C	NiHS	25	5	-	0.60	1.67	[39]
PWA-CPE	Ni/POA (TX-100)	28.5	20	6.86×10^7	0.85	1.81	This work

a) Current density: $j = I_p/A$ (A is geometric surface area of substrate).

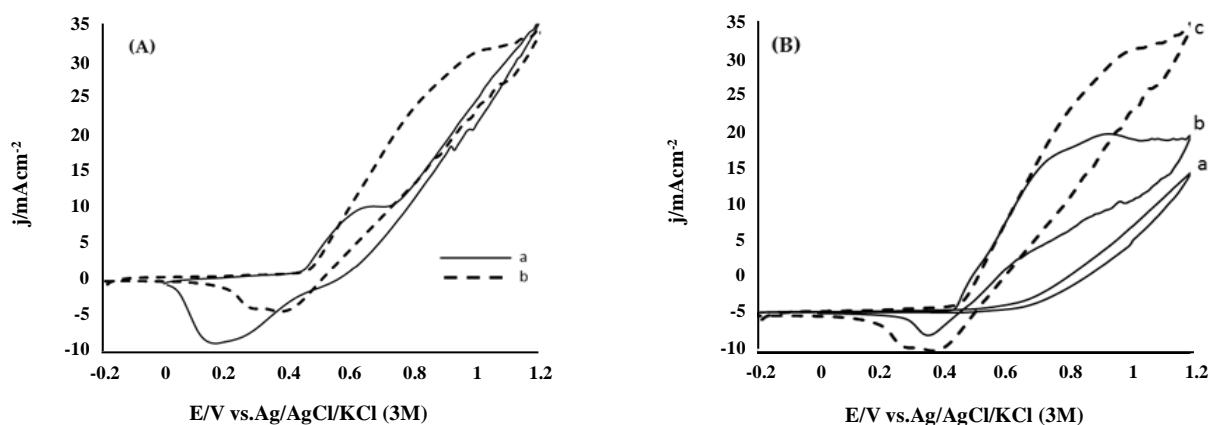


Fig. 6: (A) Electrochemical responses of the Ni/POA (TX-100)/PWA-CPE in 0.1 M NaOH in the absence (a) and the presence of 0.24 M CH₃OH (b) at $v = 20 \text{ mV/s}$. (B) CVs of (a) POA (TX-100)/PWA-CPE, (b) Ni/POA/PWA-CPE and (c) Ni/POA (TX-100)/PWA-CPE in 0.1 M NaOH + 0.24 M CH₃OH at $v = 20 \text{ mV/s}$.

CVs of methanol oxidation at Ni/POA/PWA-CPE and Ni/POA (TX-100)/PWA-CPE were shown in Fig. 6B. The Ni/POA (TX-100)/PWA-CPE produces plentiful with higher mass activity (2035 A/gNi^{-1}) than the other electrode (243 A/gNi^{-1}). Besides, the polymeric structure avoids the particle agglomerating throughout accumulation. The aim of such augmentation is the creation of a polymer film mainstay on surface of the PWA-CPE that provides the superficial arrival of methanol in the catalytic centers. In comparison with some previous works, it seems that the modified electrode can act as a similar catalyst in methanol electro-oxidation (Table 2).

The anodic current densities for methanol oxidation under the identical conditions at the surface of various electrodes were given in Fig. 7. A minor methanol

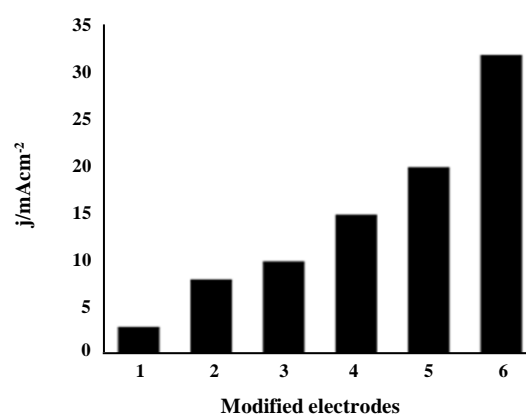


Fig. 7: Histograms of peak current density for (1) Ni/CPE, (2) Ni/POA/CPE, (3) Ni/POA(TX-100)/CPE, (4) Ni/PWA-CPE, (5) Ni/POA/PWA-CPE and (6) Ni/POA (TX-100)/PWA-CPE in 0.1 M NaOH solution containing 0.24 M methanol at $v = 0.02 \text{ V/s}$.

oxidation current is exponential in the case of the Ni/CPE. Following the dispersion of Ni on the POA/CPE, methanol oxidation happens at this electrode with higher current density. This may be credited to the presence of the polymeric film having amine groups, which increases the amount of amassed Ni. The Ni/POA (TX-100)/CPE shows higher catalytic current density than the earlier electrodes. Also, the request of PWA as incorporated material into CPE advances the electrochemical signal of methanol oxidation in alkaline medium and thus the highest current was found on the surface of Ni/POA (TX-100)/PWA-CPE.

Chronoamperometry study

Chronoamperometry was employed to investigate the electrochemical courses on the Ni/POA(TX-100)/PWA-CPE. Fig. 8A shows the double-step chronoamperograms of the electrode by setting the working electrode potential at 0.8 V (first step) and 0.47 V vs. Ag|AgCl|KCl (3 M) (second step) for several methanol concentrations. In the existence of methanol, the charge value associated with the forward chronoamperometry is superior to the backward chronoamperometry (Fig. 8B). This method can also be used for evaluation of the chemical reaction between methanol and modifier layer (catalytic rate constant, k) according to Reference 40. From the slope of I_c/I_l vs. $t^{1/2}$ plot, presented in Fig. 8C, the mean value of k for methanol concentration range from 24.0 to 96.0 mM, was found at about $6.86 \times 10^7 \text{ cm}^3/\text{mol.s}$. Table 2 compares k for the Ni/POA (TX-100)/PWA-CPE with some Ni-based modified electrodes.

Long-term stability

The electro-catalytic activity of the Ni/POA(TX-100)/PWA-CPE in methanol oxidation was examined by using electrochemical methods. At first, the stability of the electro-catalyst was checked by consecutive potential cycling in 0.1 M NaOH + 0.24 M CH₃OH (Fig. 9A). The peak current density decreases progressively by continuous potential cycling and its value at the 100th scan is about 60% of the 1st scan. For more assessment of the electro-catalytic activity of the catalysts, chronoamperograms were conducted for the Ni/PWA-CPE (a), Ni/POA/PWA-CPE (b) and Ni/POA(TX-100)/PWA-CPE (c) at 0.80 V vs. Ag|AgCl|KCl (3 M) in continuous operation (Fig. 9B). As can be seen from

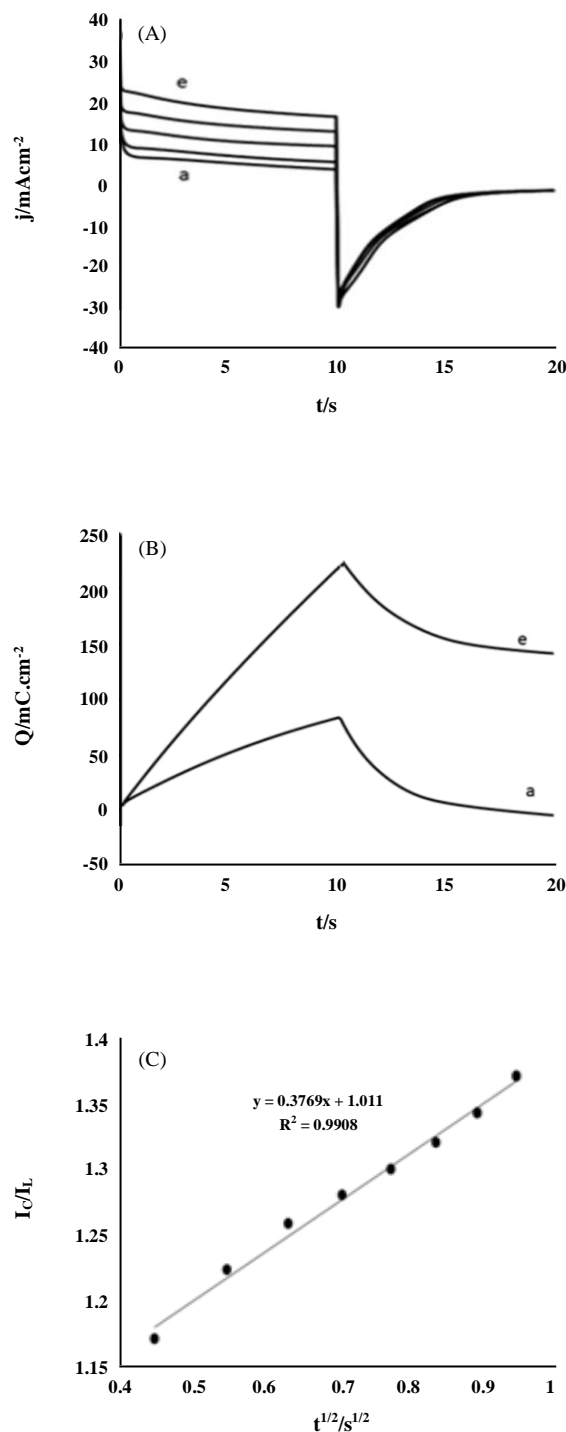


Fig. 8: (A) Chronoamperograms of the Ni/POA(TX-100)/PWA-CPE in the absence (a) and the presence of (b) 0.024, (c) 0.048, (d) 0.072 and (e) 0.096 M CH₃OH. (B) The dependency of charge Q vs. t , derived from the data of chronoamperogram of (a) and (e). (C) The dependency of I_c/I_l on $t^{1/2}$.

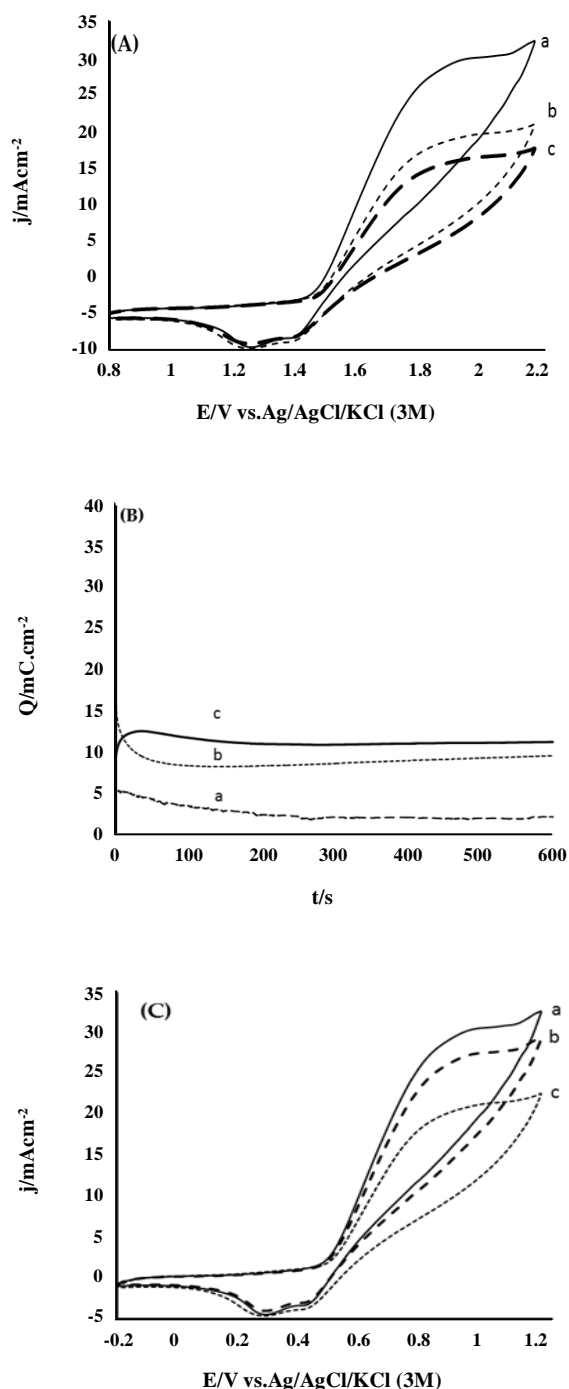


Fig. 9: (A) CVs of the Ni/POA(TX-100)/PWA-CPE in the presence of 0.24 M methanol in 0.1 M NaOH solution: 1st cycle (a); 50th cycle (b) and 100th cycle (c) at $v = 20$ mV/s. (B) Chronoamperograms of Ni/PWA-CPE (a), Ni/POA/PWA-CPE (b) and Ni/POA(TX-100)/PWA-CPE (c) in 0.24 M CH₃OH + 0.1 M NaOH solution. (C) CVs of the Ni/POA(TX-100)/PWA-CPE in 0.1 M NaOH in the presence of 0.24 M methanol at $v = 20$ mV s⁻¹: 1st day (a); 5th day (b) and 20th day (c).

this figure, the decrease in current is comparatively slow in the case of Ni/POA(TX-100)/PWA-CPE. Also, the stability of the catalyst was confirmed by measuring its response to methanol oxidation after 20 days of storage in the laboratory atmosphere conditions (Fig. 9C). The peak current density on the 20th day is about 70% of the 1st day. It seems clear that the Ni/POA(TX-100)/PWA-CPE can act as a decent catalyst in methanol oxidation.

CONCLUSIONS

The TX-100 surfactant was used as an additive for electro-polymerization of OA monomer onto the PWA-CPE in H₂SO₄ solution. The application of PWA into CPE leads to a change in the polymer growth rate. Also, TX-100 into electrolyte solution benefits the preparation of the POA with more current density. The electrochemical performance of the POA(TX-100)/PWA-CPE shows that, apart from the advanced polymerization rate in the presence of TX-100, the resulting polymer has good electrical conductivity. The Ni species onto the POA(TX-100) film shows more catalytic activity to methanol oxidation than other electrodes. The proposed electrode exhibited catalytic action towards methanol oxidation, showing reasonable stability and reproducibility when it is kept in ambient conditions or continues potential cycling.

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