

Electro-Oxidation of Ethanol and Propanol at Pt and Ti Modified Nanoparticle Substrates for Direct Alcohol Fuel Cells (DAFCs)

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Abstract: Modified Pt and Ti substrates were prepared by electrodeposition of nanocrystallite Pt and Pt_x-Sn_y catalysts for electro-oxidation of ethanol, 1-propanol and 2-propanol. The chemical composition, the phase structure and the surface morphology of the Pt and Pt_x-Sn_y electrodeposits were studied by X-ray diffractometer (XRD), energy dispersive X-ray spectroscopy (EDX) and scanning electron microscope (SEM). Their electro-catalytic activities were studied in 0.5 M H₂SO₄ by cyclic voltammetry and chronoamperometric techniques. It was found that, the nature of the substrate significantly affects the performance of the prepared catalyst towards electro-oxidation of different alcohols. Accordingly, the modified Pt substrates display enhanced catalytic activity and a higher stability towards alcohols electro-oxidation compared to the modified Ti substrates. Steady state Tafel plots experiments showed smoother and higher rate of alcohols oxidation on the modified Pt substrates than that on the modified Ti. High anodic Tafel slopes >200 for 1-propanol and 2-propanol electro-oxidation were obtained on Ti modified substrates indicating the complexity of the oxidation reaction on such electrodes.

Keywords: Electrodeposition, ethanol, 1-propanol, 2-propanol, electro-oxidation, DAFCs, electrocatalysis.

1. INTRODUCTION

Recently aliphatic alcohols have been examined as promising fuels for direct alcohol fuel cells (DAFCs) [1] in particular ethanol [2-5] and propanol [6]. This is due to the better energy efficiency, easy handling during storing and transporting [7, 8]. Ethanol is an alternative choice as a fuel due to its non-toxicity and availability from biomass resources [3, 9, 10]. Also the recent studies have focused on 2-propanol as an alcohol's fuel because it shows a lower overpotential and higher performance than methanol [8, 11, 12]. Alcohols with more than two carbon atoms have several isomers and special features of non-CO adsorption [12]. The general equation for alcohol oxidation is:



The choice of catalyst support is very important point, some authors used Ti [13, 14] and Ti mesh [15] as catalyst support and anode matrix, as the Ti would be an ideal substrate for metal deposition due to its low cost, mechanical strength and resistance to acid [16]. Other investigations [17, 18] used a Pt based catalyst for alcohols electro-oxidation and produced a Pt catalyst as nanomaterials with higher surface area for high catalytic performance and utilization efficiency [19, 20] or used Pt alloys [21]. Although Pt has been recognized as the most active electrocatalyst for alcohols oxidation [1, 22-24], but there is a drawback in that; Pt is easily poisoned by the reaction intermediate [22]. Addition of foreign metals such as Sn to the noble metals [17, 25-27] often enhances their electrocatalytic activity, where Pt promotes dehydrogenation and a second metal

addition provides oxygen at lower potentials to complete fuel oxidation to CO₂ [28-30].

On the other hand, there are only few studies devoted to a comparison between different substrate catalysts towards electrooxidation of lower molecular weight alcohols such as ethanol and propanol. The present study reports a comparison between modified Pt and Ti substrates prepared by electrodeposition technique and characterized by means of XRD, SEM and EDX analysis. The suitability and the performance of such electrodes as anodes for direct alcohol fuel cells were also investigated especially for ethanol, 1-propanol and 2-propanol by employing fundamental electrochemical methods such as cyclic voltammetry, chronoamperometry and Tafel plots.

2. MATERIALS AND METHODOLOGY

2.1. Materials

Measurements were performed on Pt and Ti sheet substrates (each has apparent surface area of 0.125 cm² and a purity of 99.99 %) modified by electrodeposited Pt and/or Pt-Sn. Chemicals were obtained from BDH (SnCl₂, H₂PtCl₆, H₂SO₄) and Analar R (ethanol, 1-propanol and 2-propanol). They were used without further purification and solutions were prepared using triply distilled water.

2.2. Electrodeposition Procedures

Before the electrodeposition process, Ti and Pt were mechanically polished using metallurgical papers of various grades, then they were subsequently degreased with acetone, rinsed with distilled water and dried with a soft tissue paper. The surface area of each electrode was calculated from the apparent area and the current density was referred to it.

The electrodeposition of Pt on Ti and/or Pt substrate electrodes was performed from 8.0 mM K₂PtCl₆ in 0.5 M

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H₂SO₄ by using the potentiostatic deposition at -530 mV vs Hg / Hg₂SO₄ / 1.0 M H₂SO₄ (MMS) for 15 minutes and the charge consumed was calculated. The amount of Pt deposited on Ti and/or Pt substrates was evaluated from the charge consumed during the electrodeposition; assuming 100 % efficiency for the following faradic reaction [31]:



The electrodeposition of Pt and Sn on Ti and/ or Pt substrates was performed from K₂PtCl₆ and SnCl₂ in 0.5 M H₂SO₄ solution by using molar ratio of 8: 1 Pt: Sn, respectively by using the potentiostatic deposition at -850 mV vs Hg / Hg₂SO₄ / 1.0 M H₂SO₄ (MMS) for 15 minutes. After the preparation of the modified Ti and Pt electrodes, no further pretreatment of the electrode was necessary to avoid any changes in the substrate surface. Real surface areas of the prepared electrodes were estimated using the charge consumed during hydrogen adsorption / desorption on the Pt surface. In order to measure the real surface area of the modified electrodes, each electrode was polarized using the cyclic voltammetric technique in 0.5 M H₂SO₄ solution from - 800 to 0 mV (MMS) at a scan rate of 50 mV s⁻¹. The area under the hydrogen oxidation peak on Pt deposits was integrated and used to calculate the real surface area of the electrode using a value of 210 μC of charge per one cm² [32, 33].

The phase structure and the crystal size of the electrodeposited particles on the surface of electrodes were studied by X-ray diffractometry (BRUKER axc-D8) using Cu k_α radiation with λ= 0.1542 nm. The scanning electron microscope (SEM) (JEOL-JSM-5410) and the energy dispersive X-ray (EDX) (EDX- Oxford) tool were used to determine the average composition ratio of Pt and Pt-Sn deposits and to examine the Pt and Pt-Sn surface morphology.

2.3. Electrochemical Measurements

Electrochemical measurements were performed on Pt and Ti electrodes of the same apparent surface area of 0.125 cm² modified by electrodeposited Pt and/or Pt-Sn and the current density was referred to this area. The electrochemical cell was described elsewhere [34]. The reference electrode is the Hg / Hg₂SO₄ / 1.0 M H₂SO₄ (MMS) (E^o = 680 mV vs NHE), and a Pt sheet was used as the counter electrode. The electrochemical measurements were performed by using Amel 5000 (supplied by Amel Instrument, Italy). The PC was interfaced with the instrument through a serial RS-232 card. Amel easyscan soft ware was used in connection with PC to control the Amel 5000 system. All the reported potentials were corrected by the positive feedback technique. All the measurements were carried out at room temperature of 25 ± 2 °C.

3. RESULTS AND DISCUSSION

3.1. Characterization of The Prepared Anodes

EDX analysis has been carried out to determine the average composition ratio of Pt and Pt-Sn electrodeposits on Ti substrates, Fig. (1a, b). The chemical content of the electrodeposits Pt and Pt-Sn are given in Table 1. Fig. (1b) and EDX analysis data show that, the position of Pt peaks is 1.967 to 2.267 KeV, and the position of Sn peak is 3.507 to

3.807 KeV, while Ti peaks are detected at the range from 4.367 to 4.668.KeV.

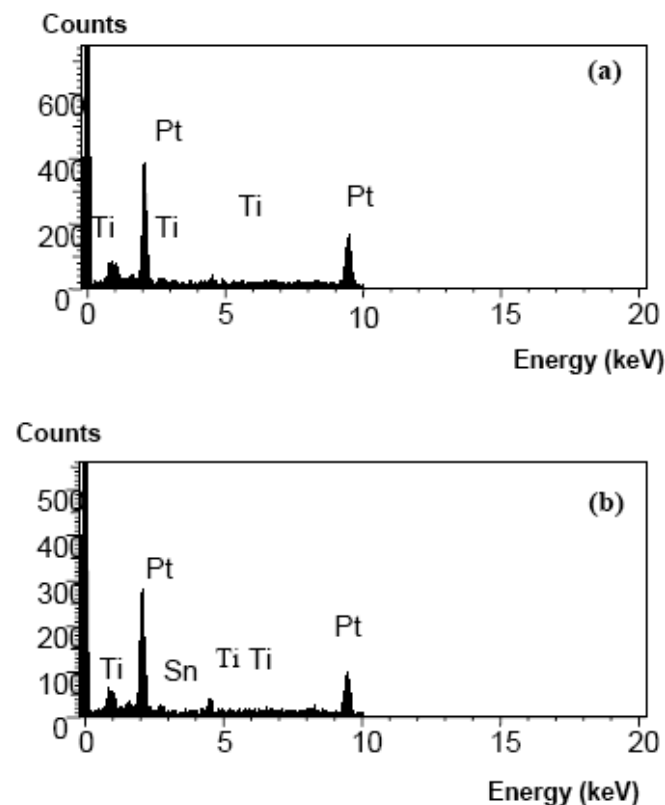


Fig. (1). EDX analysis of (a) Pt/Ti and (b) Pt-Sn/Ti.

Table 1. EDX Analysis of the Pt/Ti and Pt-Sn/Ti Modified Electrodes

Sample	Pt %	Ti %	Sn %
Pt/Ti	93.4	6.6	-
Pt-Sn/Ti (8:1)	88.1	11	0.9

SEM patterns of the Ti, Pt-Sn/Ti, Pt/Pt and Pt/Ti surfaces are shown in Fig. (2a-d). Fig. (2c, d) show an average crystal size of Pt is about 9 nm (as calculated from Scherrer equation) on both substrates, but the Pt particles are almost uniformly spread in condensed layers on the Pt substrate compared to that on the Ti substrate. The real surface area of Pt/Ti electrode is 1062 cm² and the Pt loading of this electrode is 6.5 mg per electrode area, while, the Pt loading in case of Pt/Pt is 11 mg and the real surface area of this electrode is 1371 cm². The high electric conductivity of Pt surface favors deposition of more Pt particles than the Ti surface as indicated from the SEM patterns and the amounts of Pt loading.

On the other hand, the presence of Sn with Pt changes the morphology of the electrode surface as shown in SEM pattern Fig. (2b), the surface of Pt particles appears to be covered with shiny Sn particles and the percent composition of Sn deposited is illustrated in EDX analysis Table 1. The average particle size is about 52 nm as calculated from Scherrer equation [35], therefore the presence of Sn increases the Pt particle size. The calculated real surface area

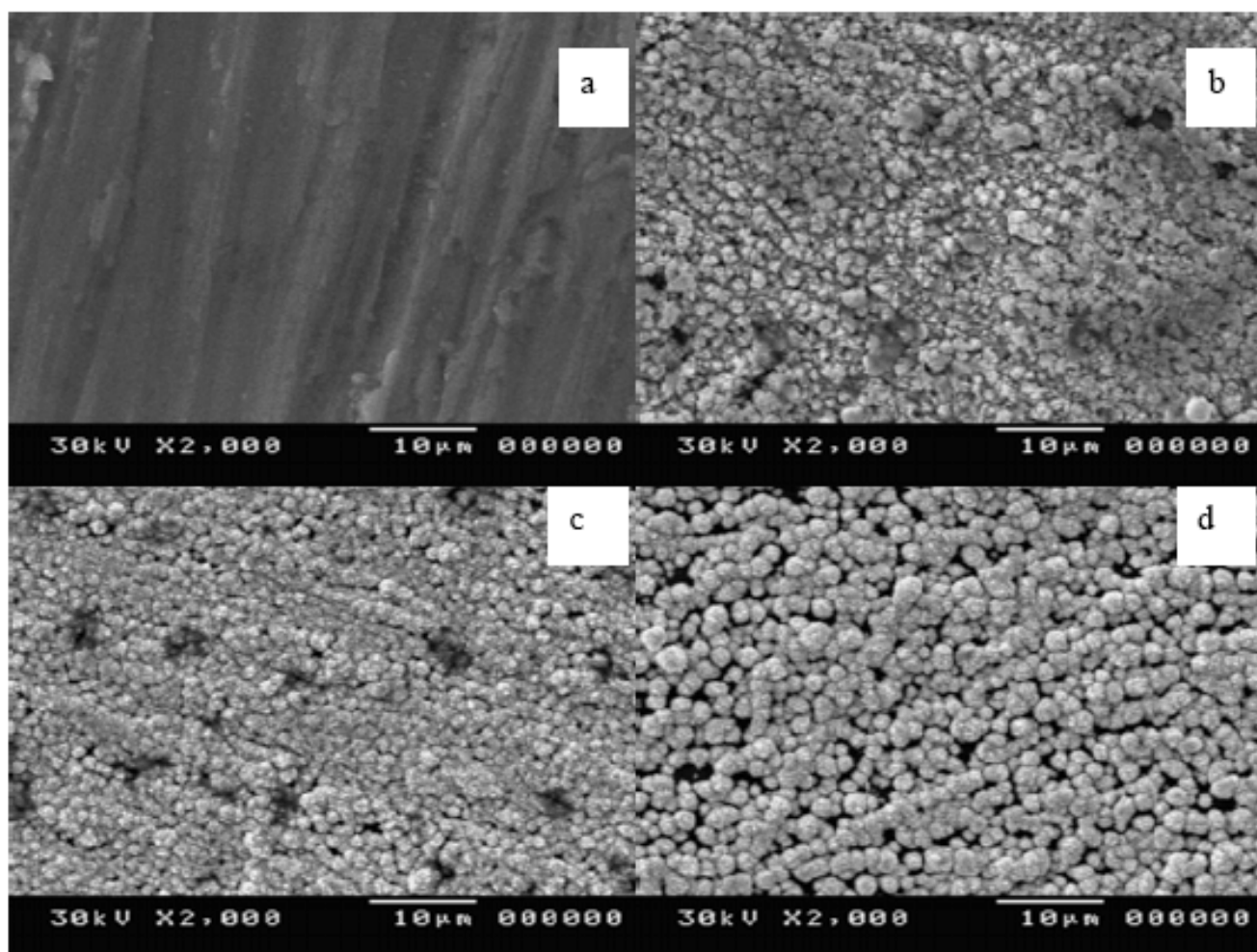


Fig. (2). SEM patterns of the (a) Ti, (b) Pt-Sn/Ti, (c) Pt/Pt and (d) Pt/Ti.

of Pt-Sn/Ti electrode is 1280 cm^2 , while the calculated real surface area of Pt-Sn/Pt is 2057 cm^2 .

Fig. (3a, b) represents XRD patterns of the Pt/Ti and Pt-Sn/Ti electrodes. Diffraction pattern of Pt shows five sharp peaks with different intensities and few small peaks corresponding to TiO_2 are illustrated in Fig. (3). The sharp peaks illustrate a crystalline structure pattern of the prepared catalysts. The grain size of Pt particles deposited on substrate surfaces can be estimated by the Scherrer equation [35]:

$$t = \frac{0.9\lambda}{B \cos(\theta_B)} \quad (3)$$

where $\lambda = 0.1542 \text{ nm}$ is Cu (k_α) wave length, B is the broadening of the full width at half maximum (F.W.H.M). The phase composition investigations of Pt/Ti reveal the presence of two phases (Fig. 3). The calculated grain size from the Scherrer formula is based on the highest five diffracted peaks of Pt.

3.2. Electrooxidation of Ethanol

Fig. (4a-d) shows the blank cyclic voltammograms of Pt/Pt, Pt-Sn/Pt, Pt/Ti and Pt-Sn/Ti electrodes in $0.5 \text{ M H}_2\text{SO}_4$ at a scan rate of 50 mV/s . In all cases, the polarization was

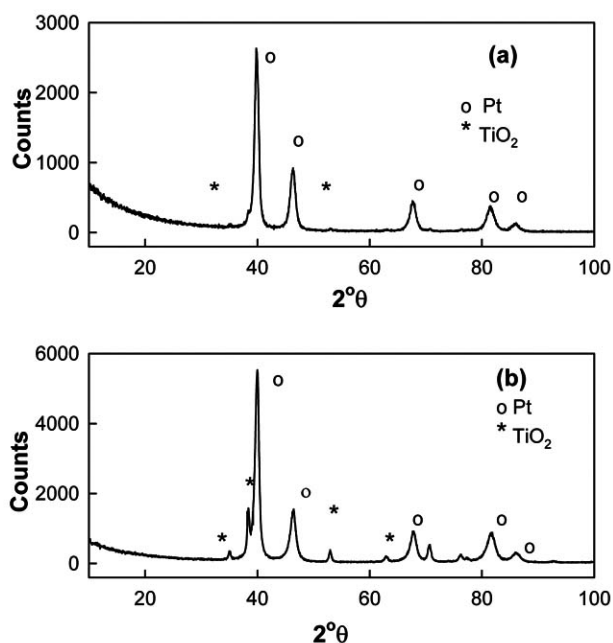


Fig. (3). XRD patterns of the (a) Pt/Ti and (b) Pt-Sn/Ti.

started at -500 mV up to +1400 mV or +1200 mV (MMS) in the anodic direction, then the scan was reversed to -500 mV in the cathodic direction. Similar cyclic voltammograms are displayed for all the studied electrodes but with different current densities. The characteristic features of the peaks indicating hydrogen adsorption / desorption and oxide formation / stripping peaks take place at the starting of the cyclic voltammograms in the potential range from -300 to -100 mV (MMS). The oxygen evolution takes place at relatively high positive potential in the anodic direction, in addition to another reduction peak in the cathodic direction near to 300 mV (MMS) due to the Pt oxides reduction. The Sn addition in case of Pt-Sn/Pt or Pt-Sn/Ti increases the current of hydrogen adsorption and desorption than the Pt alone, thus it could increase the roughness factor of the Pt surface [36], consequently increasing the catalytic activity of the prepared electrodes. The area under the hydrogen adsorption / desorption peaks are integrated and used to calculate the real surface area of the prepared electrodes as mentioned above.

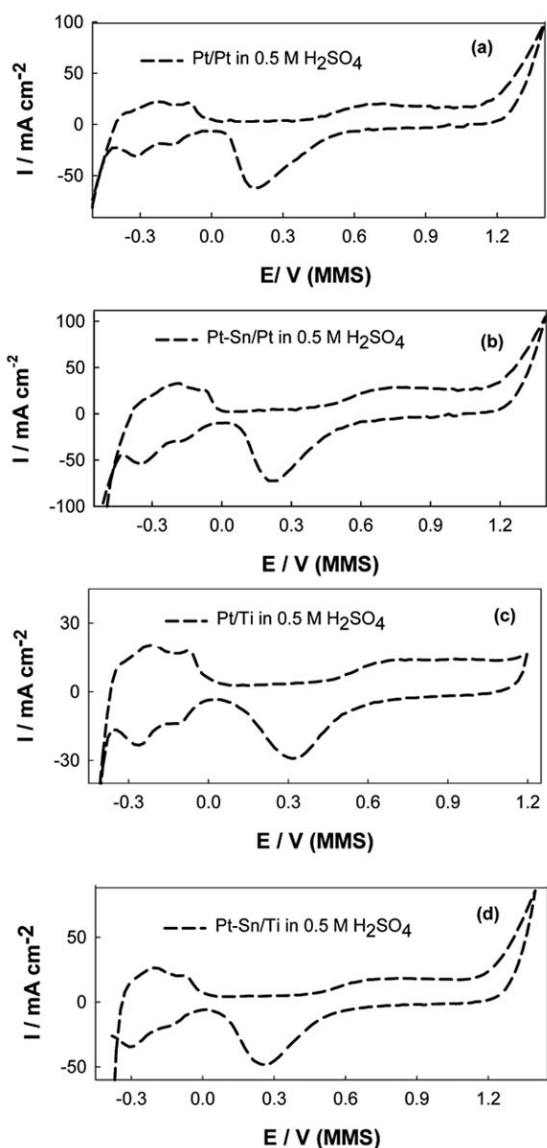


Fig. (4). Blank cyclic voltammograms of (a) Pt/Pt, (b) Pt-Sn/Pt, (c) Pt/Ti and (d) Pt-Sn/Ti electrodes in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹.

Cyclic voltammograms of electro-oxidation of ethanol at the modified Pt/Pt and Pt/Ti electrodes are represented in Fig. (5a, c). In presence of 2.0 M ethanol, the solid lines in Fig. (5a, c), indicate an oxidation peak at about + 819 mV (MMS) of 112 mA cm⁻² at a Pt/Pt electrode and at +658 mV (MMS) of 112 mA cm⁻² oxidation current density at a Pt/Ti electrode in the forward direction and another reoxidation peak appeared in the reverse direction in both cases probably due to the removal of carbonaceous species not completely oxidized in the forward scan [37, 38]. The multiple re-oxidation peaks indicate the complexity of the adsorbed reaction intermediates [22]. Taking into consideration the real surface area of each electrode, one can see that, the oxidation current density of ethanol on a Pt/Ti is higher than that on a Pt/Pt electrode. But the stability of Pt/Pt electrode over repeated cyclization is higher than that of a Pt/Ti electrode, it reaches 73 % after 20 cycles for the first electrode and 53 % for the second [the dotted lines in Fig. (5a, c)]. The final products of ethanol electro-oxidation depend on the applied potential, CO₂ [24, 39] in addition to methane and ethane have been detected as products of ethanol electro-oxidation [40]. Complete oxidation to CO₂ is a minority pathway at all potentials [24], as it involves the cleavage of C-C bond [41]. Adsorbed CO is also identified on pure Pt [9] in addition to other surface intermediates including various C₁ and C₂ small molecular species such as ethoxy and acetyl [40, 42]. Complete ethanol electro-oxidation involves 12 electrons per molecule and more intermediates and products than that of methanol. Therefore pure Pt is not a very good anode catalyst for ethanol oxidation as it is readily poisoned by the strongly adsorbed intermediates e.g. CO_{ad} [43].

On the other hand, addition of a small amount of Sn improves the catalytic activity and the stability of the prepared electrodes. It was found that [44] addition of Sn to Pt inhibits the decomposition of ethanol to CO, CH₄ and C₂H₆ owing to the suppression of C-C bond cleavage so it reduces the poisoning by CO [9]. Electro-oxidation of ethanol at Pt-Sn/Pt exhibited a higher oxidation current than that at Pt/Pt and the stability of the electrode over repeated cyclization is also improved, as illustrated in Table 2. Also, the Pt-Sn/Ti electrode is superior to Pt/Ti electrode Fig. (5b, d). Over repeated potential cyclization up to 20 cycles the oxidation peak current density reached 77 % of the current density of the first cycle for the Pt-Sn/Pt and 63 % for the Pt-Sn/Ti electrode. This indicates that, not only the oxidation of ethanol occurs at high current density, but also the stability of the electrode over repeated cyclization is improved in presence of Sn. The role of Sn in enhancing the catalytic oxidation of alcohol is attributed to its ability to supply surface oxygen containing species required for the oxidative removal of CO like species strongly adsorbed on adjacent Pt active sites [45-47]. Mehandru *et al.* [48] found that by using thermal desorption spectra (TDS) CO dissociates on Pt-Ti alloys easier than on pure Pt, so the behavior of Pt-Sn alloys could be qualitatively similar to the Pt-Ti alloys. Moreover, Sn promotes the electro-catalytic activities for the electro-oxidations of alcohol, as it causes significant structural and electronic modifications of Pt crystallites, resulting in an increase of lattice parameter and a decrease of the Pt 5d band vacancies with Sn content [16, 49]. Moreover, Sn favors the

oxidation of ethanol to acetaldehyde and acetic acid leading to larger oxidation currents [26, 28].

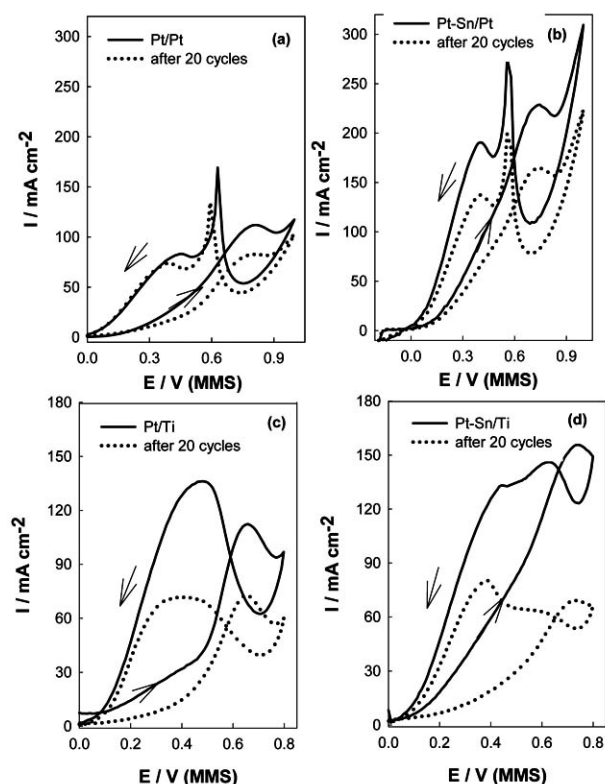


Fig. (5). Cyclic voltammograms of (a) Pt/Pt, (b) Pt-Sn/Pt, (c) Pt/Ti and (d) Pt-Sn/Ti electrodes in 0.5 M H₂SO₄+ 2.0 M ethanol (the solid lines) and after 20 cycles (the dotted lines) at a scan rate of 50 mV s⁻¹.

Table 2. The Oxidation Peak Current Density, the Peak Potential and the Efficiency After 20 Cycles of Ethanol Oxidation at Different Modified Electrodes

Sample	I _p / mA cm ⁻²	I _p mA/ Real Surface Area	E _p / mV (MMS)	Efficiency After 20 Cycles
Pt/Pt	112	0.082	819	73
Pt/Ti	112	0.105	658	53
Pt-Sn/Pt	221	0.107	840	77
Pt-Sn/Ti	155	0.121	743	63

Table 2 summarized that ethanol electro-oxidation occurs at a relatively low potential and low oxidation current at the Pt/Ti and Pt-Sn/Ti compared to the Pt/Pt and Pt-Sn/Pt electrodes. The apparent enhancement that was obtained with a Pt/Pt or Pt-Sn/Pt electrode is attributed to the increase of the real surface area of Pt deposited on Pt relative to the Pt deposited on Ti. This is due to the electronic nature of Pt and its high electric conductivity relative to the surface of Ti which favors deposition of more Pt deposits on its surface, (the amount of Pt loading in case of Pt/Pt is 11 mg and 6.5 mg for Pt/Ti at the same time of deposition and the same apparent surface area of both substrates). When the oxidation current is normalized to the real surface area of each

electrode, the oxidation current density of ethanol at a Pt/Ti and/or a Pt-Sn/Ti electrode is about 1.3 times greater than that at a Pt/Pt and/or a Pt-Sn/Pt electrode. This is attributed to the effect of the bimetallic catalysts. It is known that, oxidation of alcohol on a Pt occurs due to the presence of oxygenated species (PtO or PtOH), which help the oxidation of CO to CO₂. Therefore the objective of research on bimetallic catalysts is to find a metal that can adsorb the OH radical or any other oxygen containing species at relatively lower potentials [50]. Alloying element (metal) facilitates the adsorption of oxygen containing species such as OH_{ads} [51, 52]. Pt-OH reacts with organic poison. Also, the enhancement may occur by preventing the formation of a strongly adsorbed poisoning species such as CO either by blocking the sites necessary for its adsorption [53] or by oxidizing completely CO in solution into CO₂ [54]. Ti metal can perhaps achieve these goals. An extended Hückel calculation of the Pt-Ti bonding [55] illustrated filling of the d-band by donation of d-electrons from Ti to unfilled Pt d-orbital that makes decreasing in binding of CO to Pt (this donation occurs even with an oxygen bound to the Ti site). The donation should make Ti even more electropositive, binding oxygen even more strongly than the pure metal. Accordingly, a high catalytic activity of the modified Ti substrate relative to that of the modified Pt substrate towards ethanol electro-oxidation can be suggested.

3.3. Electrooxidation of 1-Propanol

Fig. (6a, d) illustrates the cyclic voltammograms of electro-oxidation of 1-propanol at the modified Pt/Pt, Pt/Ti, Pt-Sn/Ti and Pt-Sn/Pt electrodes. In presence of 2.0 M 1-propanol, the solid lines in the figures indicate that oxidation of 1-propanol occurs at relatively low potential at the modified Ti electrodes relative to the modified Pt electrodes, but the oxidation current density of 1-propanol is higher at Pt modified electrodes than that at Ti modified electrodes, in addition the stability of the modified Pt electrodes over repeated cyclization is higher than that of the Ti modified electrodes, the values of oxidation current density, the peak potential and the efficiency after 20 cycles for each electrode are illustrated in Table 3. Taking into consideration the real surface area of each electrode, it was found that the oxidation current density of 1-propanol at modified Pt substrates is greater than that at modified Ti substrates. This is due to the complexity of the oxidation reaction on Ti substrates relative to that on Pt substrates as indicated from Tafel plots in the following section (Fig. 6b). Propanal, propionic acid and CO₂ are the main products of 1-propanol oxidation [12].

Table 3. The Oxidation Peak Current Density, the Peak Potential and the Efficiency After 20 Cycles of 1-Propanol Oxidation at Different Modified Electrodes

Sample	I _p / mA cm ⁻²	I _p mA/ Real Surface Area	E _p / mV (MMS)	Efficiency After 20 Cycles
Pt/Pt	55	0.040	703	49
Pt/Ti	40	0.038	679	28
Pt-Sn/Pt	121	0.059	666	86
Pt-Sn/Ti	57	0.045	687	47

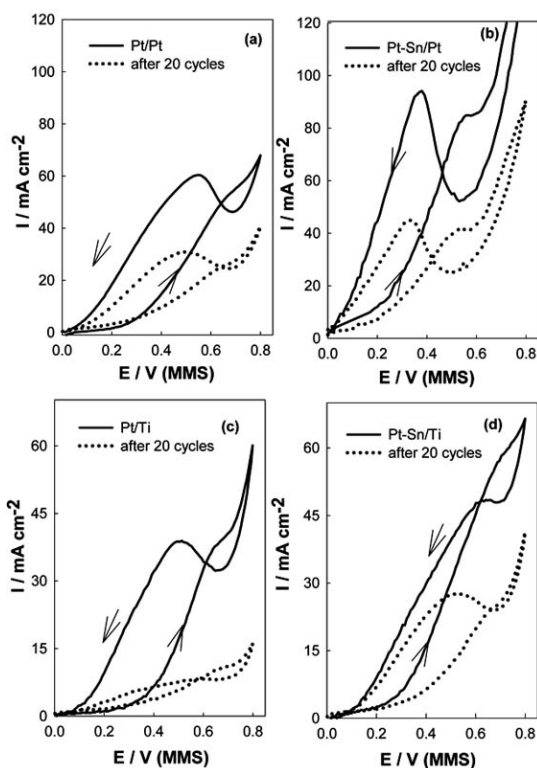


Fig. (6). Cyclic voltammograms of (a) Pt/Pt, (b) Pt-Sn/Pt, (c) Pt/Ti and (d) Pt-Sn/Ti electrodes in 0.5 M H_2SO_4 + 2.0 M 1-propanol (the solid lines) and after 20 cycles (the dotted lines) at a scan rate of 50 mV s^{-1} .

3.4. Electrooxidation of 2-Propanol

Cyclic voltammograms of electro-oxidation of 2-propanol at the modified Pt/Pt, Pt/Ti, Pt-Sn/Ti and Pt-Sn/Pt electrodes are represented in Fig. (7a-d). In presence of 2.0 M 2-propanol, the solid lines in the figures indicate that the oxidation of 2-propanol occurs at relatively low potential at the modified Ti electrodes (Fig. 7c, d) relative to the modified Pt electrodes (Fig. 7a, b), while the oxidation current density of 2-propanol is higher at Pt modified electrodes compared to the Ti modified electrodes, in addition the stability of the modified Pt electrodes over repeated cyclization is higher than that of the Ti modified electrodes (Table 4). The main product in the oxidation of 2-propanol is acetone due to the difficult breaking of C-C bond [38], in addition to CO_2 [12]. Oxidation of 2-propanol involves 18 electron transfers, so the process is very complicated, also, it displays the multiple oxidation peaks especially on the modified Ti substrates and multiple re-oxidation peaks which indicates the complexity of the adsorbed reaction intermediates [17].

Table 4 summarized that 2-propanol electro-oxidation occurs at a relatively low potential at Pt/Ti and Pt-Sn/Ti with a relatively small oxidation current density, compared to Pt/Pt and Pt-Sn/Pt electrodes. Taking into consideration the real surface area of each electrode, the oxidation current density of 2-propanol at Pt modified electrodes is higher than that at Ti modified electrodes. Moreover, Pt modified

electrodes display higher stability over repeated cyclization than the Ti modified electrodes.

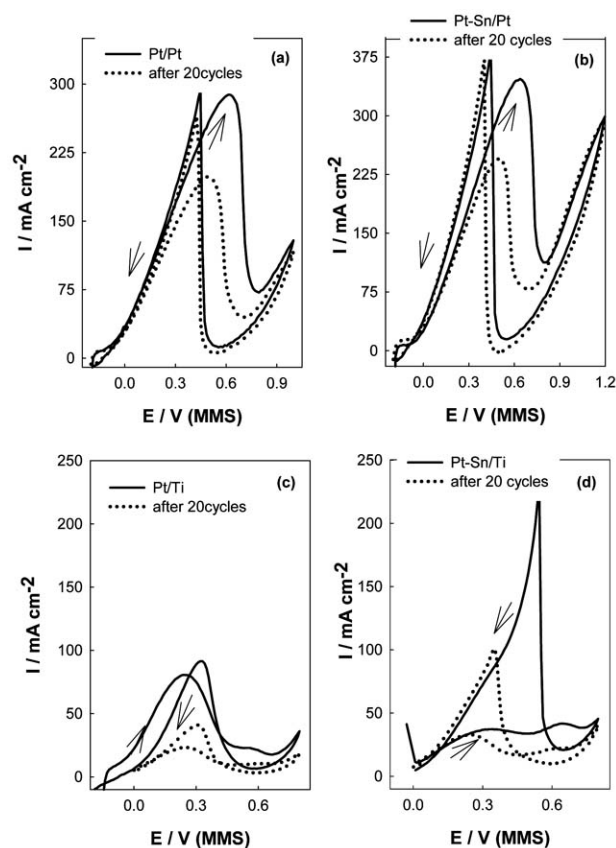


Fig. (7). Cyclic voltammograms of (a) Pt/Pt, (b) Pt-Sn/Pt, (c) Pt/Ti and (d) Pt-Sn/Ti electrodes in 0.5 M H_2SO_4 + 2.0 M 2-propanol (the solid lines) and after 20 cycles (the dotted lines) at a scan rate of 50 mV s^{-1} .

Table 4. The Oxidation Peak Current Density, the Peak Potential and the Efficiency After 20 Cycles of 2-Propanol Oxidation at Different Modified Electrodes

Sample	$I_p / \text{mA cm}^{-2}$	$I_p \text{ mA} / \text{Real Surface Area}$	$E_p / \text{mV (MMS)}$	Efficiency After 20 Cycles
Pt/Pt	291	0.212	626	68
Pt/Ti	22	0.021	579	47
Pt-Sn/Pt	346	0.169	638	70
Pt-Sn/Ti	41	0.032	655	56

A trial to satisfy the obtained results and also to clarify the stabilities of the various prepared electrodes towards electro-oxidation of different alcohols, the chronoamperometric experiments for Pt/Pt, Pt/Ti, Pt-Sn/Pt and Pt-Sn/Ti electrodes were performed at +800 mV (MMS) and represented in Fig. (8a-c) for all the studied alcohols at 2.0 M concentration in 0.5 M H_2SO_4 . From the figure it is clear that, the stability decreases in the order of Pt-Sn/Pt > Pt/Pt > Pt-Sn/Ti > Pt/Ti for all the studied alcohols. This is due to the complexity of the oxidation reaction on Ti substrates that was indicated by the multiple oxidation and reoxidation peaks in the cyclic

voltammogram especially in case of 2-propanol and the complexity of reaction intermediates that are adsorbed on the electrode surface thus decreasing its stability with time.

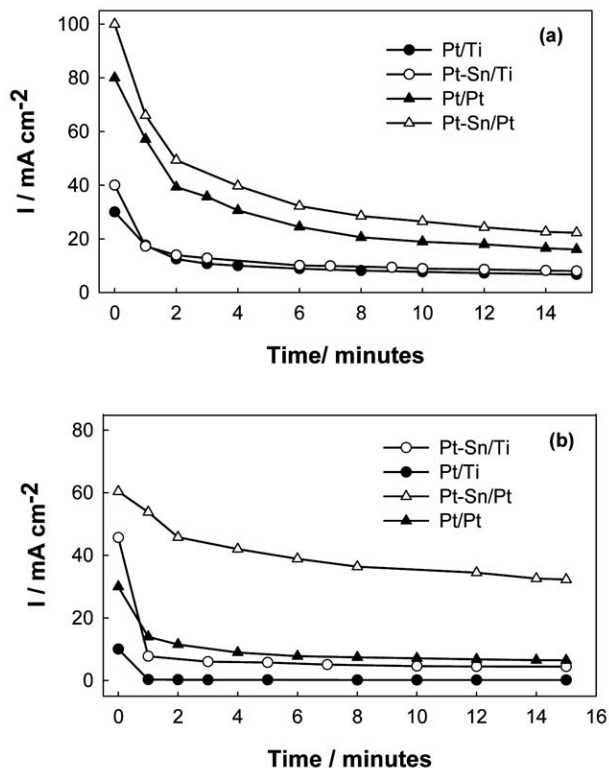


Fig. (8). Chronoamperometric data of the Pt/Ti, Pt/Pt, Pt-Sn/Pt and Pt-Sn/Ti at +800 mV (MMS) in 0.5 M H₂SO₄ and 2.0 M alcohol (a) ethanol and (b) 1-propanol.

To shed light on the facility of the oxidation process on both substrates, anodic Tafel plots for ethanol, 1-propanol and 2-propanol on Pt modified electrodes (Pt/Pt and Pt-Sn/Pt) and on Ti modified electrodes (Pt/Ti and Pt-Sn/Ti) in 0.5 M H₂SO₄ at 1.0 mV s⁻¹ were studied. Fig. (9a, b) represents Tafel plots for ethanol and 1-propanol only for simplicity. Table 5 summarized the electrochemical parameters that derived from all Tafel plots and it shows that, anodic Tafel slopes of 101-130 mV decade⁻¹ were obtained for ethanol electro-oxidation at the Pt modified electrodes (Pt/Pt and Pt-Sn/Pt) suggest the same reaction mechanism at both electrodes, and 81-118 mV decade⁻¹ were estimated on Ti modified electrodes (Pt/Ti and Pt-Sn/Ti) also suggesting the same reaction mechanism. Also it indicates a facile mechanism and a higher rate of ethanol electro-

oxidation on modified Pt electrodes indicated by high anodic oxidation current density (*i_a*) than that on Ti modified electrodes, while anodic oxidation of 1-propanol and 2-propanol shows high anodic Tafel slopes *b_a* > 200 and low anodic oxidation current densities (*i_a*) at Ti modified electrodes indicating a lower reaction activity [14] and complexity of the oxidation process on Ti modified electrodes compared to that on the Pt modified electrodes.

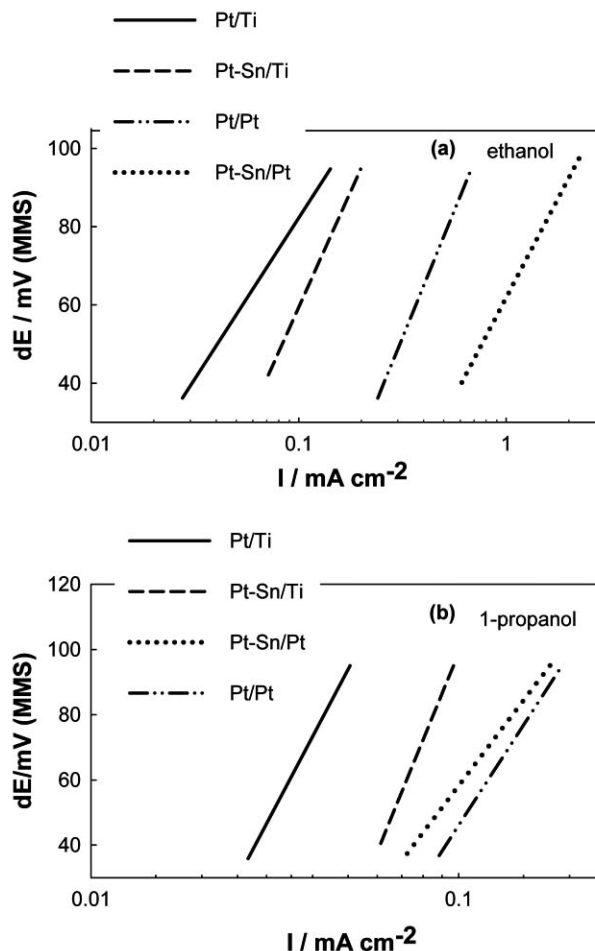


Fig. (9). Anodic Tafel lines for 2.0 M (a) ethanol and (b) 1-propanol at Pt/Pt, Pt/Ti, Pt-Sn/Pt and Pt-Sn/Ti electrodes in 0.5 M H₂SO₄ at 1.0 mV s⁻¹.

4. CONCLUSION

The electro-oxidation of ethanol, 1-propanol and 2-propanol was studied on Pt and Ti modified substrates in H₂SO₄ medium. The results show that the performance of the

Table 5. Electrochemical Parameters (The Anodic Oxidation Current *i_a* and Anodic Tafel Slope *b_a*) Derived from Anodic Tafel Plots for Ethanol, 1-Propanol and 2-Propanol Oxidation at Different Modified Electrodes

Sample	<i>i_a</i> /mA cm ⁻² for Ethanol	<i>b_a</i> mV/dec for Ethanol	<i>i_a</i> /mA cm ⁻² for 1-Propanol	<i>b_a</i> mV/dec for 1-Propanol	<i>i_a</i> /mA cm ⁻² for 2-Propanol	<i>b_a</i> mV/dec for 2-Propanol
Pt/Pt	0.148	130	0.055	177	0.080	114
Pt/Ti	0.016	81	0.020	213	0.021	215
Pt-Sn/Pt	0.236	101	0.040	148	0.047	125
Pt-Sn/Ti	0.030	118	0.045	275	0.027	277

modified Pt substrate is better than that of the modified Ti towards alcohols electro-oxidation, this is due to its good surface electric conductivity relative to the surface of Ti. The stability of the modified Pt substrates is higher than that of the modified Ti. Also, an easier mechanism and higher rate for alcohols electro-oxidation are found with the Pt modified electrodes compared to the Ti modified electrodes. High anodic Tafel slopes are obtained with 1-propanol and 2-propanol oxidation at Ti substrates indicate the complexity of the reaction at such electrodes. Addition of a small amount of Sn deposited with Pt either on Pt or Ti substrates improves the catalytic activity and the stability of fabricated electrodes towards alcohols electro-oxidation.

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