



Titanium and platinum modified titanium electrodes as catalysts for methanol electro-oxidation

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ABSTRACT

Electro-oxidation of methanol was studied on titanium and platinum modified titanium electrodes (Pt/Ti). Platinum was electro-deposited on Ti by potentiostatic and galvanostatic techniques. Electrodes prepared by the galvanostatic technique showed enhanced catalytic activity towards methanol oxidation in NaOH solution compared to those prepared by the potentiostatic method. Scanning electron microscopy and energy dispersive X-ray analysis were used to characterize the surface morphology and percent composition of Pt to Ti on the electrode surface. The catalytic activity of Pt/Ti electrode is much higher than that of Pt/Pt, bulk Ti and of pure Pt, in addition to minimizing the poisoning effect. In 3.0 M NaOH and in the presence of 2.0 M MeOH, the oxidation peak current density value of methanol after the 50th cycles reached 99.4% of its value at the first cycle for electrodes prepared by the galvanostatic method compared to 94.7% for electrodes prepared by the potentiostatic method. Polarizing the modified electrode at the hydrogen evolution potential region for a certain time was found to enhance the catalytic oxidation of methanol, while the presence of thick Ti-oxide as well as Ti-hydride inhibited the process.

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1. Introduction

In recent years, Ti and TiO₂ electrodes have been used as anodes or cathodes for some electrochemical reactions of technological interest such as oxygen and chlorine evolution reactions and the reduction of oxygen [1]. It has been reported that, the electro-catalytic properties of Ti/TiO₂ electrodes can be improved by doping the oxide film with noble metals like Pt [2–9]. The Pt/TiO₂ composite can be synthesized in various ways such as electrochemical [10], electrodeless deposition [11], thermal decomposition [12], etc. The deposition of Pt on Ti can be realized either by direct deposition on the oxide film or on the oxide free surface. It was reported that Ti would be an ideal substrate for metals deposition due to its low cost, mechanical strength and resistance to acid [13].

Electro-oxidation of methanol was studied on Pt finely dispersed on TiO₂ [14] and Ti metal [15]. The dispersion was studied on freshly polished Ti at open circuit, and the hydrogen evolution reaction was used as a probe reaction for testing both the catalytic activity and deposition conditions. On Ti covered by a thin oxide film, the rate of deposition is very low [11]. In case of Ti supported nanostructure Pt electrodes, it was observed that their electrochemical activities were much higher than that of the bulk Pt electrode [16]. Rasko et al. [17] used powdered TiO₂ and Pt/TiO₂ for the catalytic oxidation of formaldehyde. In comparison with the conventional hot pressed

carbon supported Pt catalysts, highly dispersed Pt deposited over the Ti mesh showed higher electro-catalytic activity towards methanol oxidation with a stable performance [12]. The oxidation activity increased with pH or OH coverage of the electrode surface. A reaction order of close to 0.5 with respect to OH⁻ was observed in the presence of methanol in alkaline solution. The adsorption of methanol and OH⁻ on the platinized Ti electrode follows Temkin isotherm [18].

The nanostructure electrode consisting of Pt nanophases and a titanium oxide matrix was fabricated by means of co-sputtering deposition method and used for methanol oxidation in methanol fuel cells [19]. The electrode showed a remarkably enhanced performance for methanol oxidation under UV illumination compared to that without UV illumination. TiO₂ and Ti coated with oxides of several other metals; Pt, Au, Fe, Co, Ni, Mo, Mn, Cr, Cu and Hg or their combinations Sb–Sn, Co–Mn, Ni–Si, Ni–Cr–Mo and Fe–Cr [20,21] are also used for methanol electro-oxidation. Pt/Ti and Pt/TiO₂ electrodes were also made by galvanic deposition of platinum metal [22] and used for the electro-oxidation of glycerol. The results indicated the good electrical conductivity of and connectivity between the deposited platinum and substrates and hence the absence of any significant resistive surface oxide film. Titanium-supported nanoporous network bimetallic Pt–Ir/Ti electrocatalysts have been fabricated by the hydrothermal process [23]. They exhibit the highest electrocatalytic activity towards the formic acid oxidation in 0.5 M H₂SO₄. The catalysts Pt and PtRu, deposited on supporting nanoporous TiO_{2-x} films, were used to study methanol oxidation reaction [24]. A lower poisoning effect for cluster PtRu on a TiO_{2-x} support film than that for unsupported PtRu or bare Pt catalysts has been observed. These effects have been attributed to differences in

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CO_{ad} binding energy and lowering of activation energy for surface mobility leading to a more facile 2D diffusion of CO_{ad} from Pt sites to Ru and the supporting TiO_{2-x} .

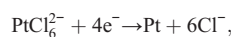
It was found that, the texture of Ti electrodes affects the oxidation rate [25]. A 50–50 ordered Ni–Ti alloy was found to be more active than Ni or Ti electrodes for methanol oxidation in acidic medium due to the formation of a passivating layer, which suppresses the nickel corrosion [26]. Ti/RuO₂ films modified with Pt nanoparticles were prepared by the sol–gel technique and used for oxygen evolution reaction by very slow potential sweeps and chronoamperometry. It exhibits fairly good electrocatalytic activity towards the oxygen evolution reaction [27]. On the other hand, RuO₂/TiO₂ nano-tubes and nanoparticles composite electrodes were used for CO₂ reduction. Compared with RuO₂ and RuO₂/TiO₂ nanoparticles composite electrodes, RuO₂/TiO₂ nanoparticles composite modified Pt electrode had higher electrocatalytic activity for the electrochemical reduction of CO₂ to methanol [28]. The performance of composite oxides on Ti is comparable to or better than the use of oxides grown on a noble substrate [29].

The aim of the present investigation is to prepare dispersed Pt particles on Ti and studying the electro-catalytic activity of the formed surface towards methanol electro-oxidation in NaOH solution. The effect of TiO₂ and titanium hydride, formed electrochemically, and their thickness on the methanol oxidation process was also studied on Ti and Ti modified with Pt particles.

2. Experimental techniques

Electrochemical measurements were performed on Ti electrodes of 99.6% purity and on a Ti modified by electrodeposited Pt. The geometric surface area of Ti electrode is 0.125 cm² which was used to calculate the current density values. The electrochemical cell was described elsewhere [30]. The reference electrode to which all potentials are referred is the Hg/HgO/1.0 M NaOH (MMO, E°=0.140 V versus NHE). Another reference electrode, Hg/Hg₂SO₄/1.0 M H₂SO₄ (MMS, E°=0.680 V versus NHE) was used in the experiments of the electrochemical deposition of Pt on Ti. A platinum sheet was used as the counter electrode. Measurements were carried out at room temperature. All chemicals used in this work were reagent grade products and used as received without further purifications. Triply distilled water was used throughout for the preparation of solutions.

Before the electrodeposition of Pt, Ti was mechanically polished using metallurgical papers of various grades, then it was subsequently degreased with acetone, rinsed with distilled water and dried. The electrodeposition of Pt on Ti electrodes was performed potentiostatically from a solution composed of 8.0 mM K₂PtCl₆ in 0.5 M H₂SO₄ at –530 mV (MMS) for 5.0 min. The amount of the charge consumed during the electrodeposition process was simultaneously recorded. In another set of experiments the time of the deposition was varied from 1.0 up to 20 min in order to deposit more Pt and the amount of charge was recorded in each case. Another method of deposition was also performed using the galvanostatic technique at a constant current of –1.0 mA for different time intervals. After the preparation of Pt modified Ti electrodes, no further pretreatment of the electrode was necessary to avoid any changes in the substrate surface. The amount of Pt deposited on Ti electrodes (Pt loading) in each case was evaluated from the charge consumed during the electrodeposition; assuming that, the quantity of charge is mainly due to the following faradic reaction [31]:



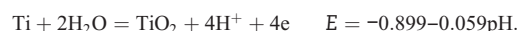
and any other side reactions are considered negligible under the given experimental conditions [31]. On the other hand, the real surface area of the modified electrode was measured using the charge consumed

during hydrogen desorption on the Pt electrode surface [32]. In order to measure the real surface area of the modified electrode, it was polarized using the cyclic voltammetric technique in 0.5 M H₂SO₄ solution from –0.80 to –0.3 V (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]. The authors are aware with the fact that titanium also is strongly electro-active in the potential range of hydrogen evolution. Therefore, the estimation of the real surface area of the electro-deposited Pt from the data of the hydrogen desorption charge during the polarization of the modified electrode in 0.5 M H₂SO₄ solution is only use for comparison.

Scanning electron microscopy and energy dispersive X-ray analysis were used to examine the Pt distribution on the surface of Ti electrodes prepared by the above mentioned methods and provide estimation about the percent of Pt to Ti exist on the electrode surface. The electrochemical measurements were performed by cyclic voltammetric technique using Amel 5000 (supplied by Amel Instrument, Italy) driven by a pc for data processing. The pc was interfaced with the instrument through a serial RS-232 card. Amel Easyscan software was used in connection with pc to control the Amel 5000 system. All the reported potentials were corrected by the positive feedback technique.

3. Results and discussion

Anodization of Ti in alkaline, neutral and moderately acidic aqueous media resulted in the formation of a thermodynamically stable oxide film, TiO₂, according to the following equation [33]:



The oxide film (TiO₂) formed on the metal surface is known to be compact and poorly conducting. Fig. 1a represents the cyclic voltammogram of a mechanically polished Ti electrode in 0.5 M

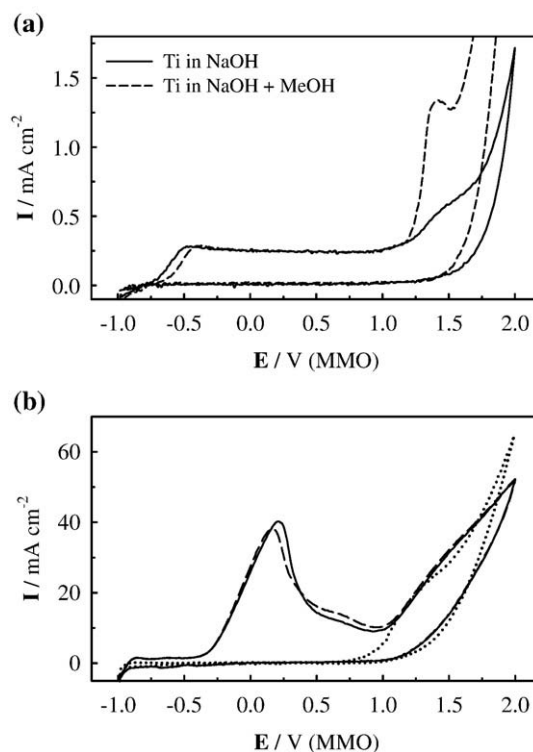


Fig. 1. Cyclic voltammograms at a scan rate of 50 mV s^{–1} of (a) Ti electrode and (b) Pt/Ti electrodes, in 0.5 M NaOH (.....) and in NaOH containing 4.9 M MeOH: (–) 1st cycle, and (– –) 5th cycle.

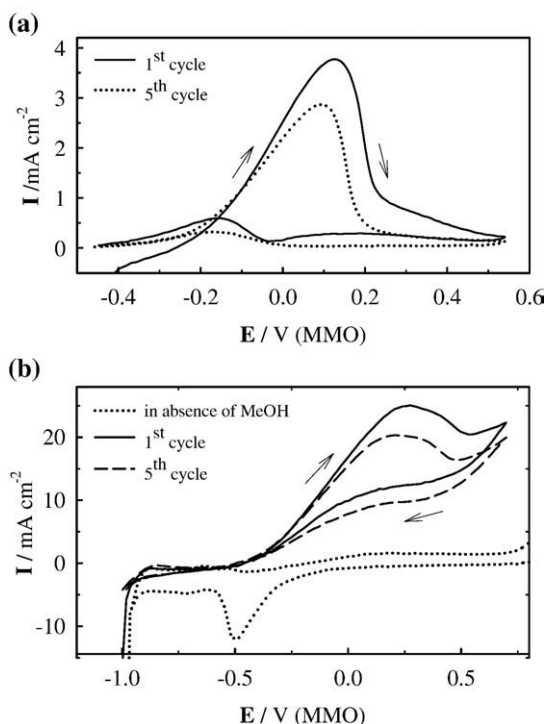
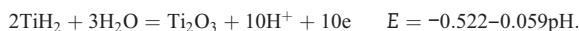
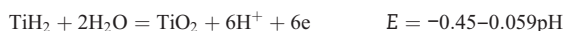


Fig. 2. Cyclic voltammograms in 0.5 M NaOH solution containing 4.9 M MeOH at a scan rate of 50 mV s⁻¹ for: (a) Pt electrode; (b) Pt/Pt electrode (Pt was deposited on Pt potentiostatically at -530 mV (MMS) for 5 min).

NaOH solution recorded from -1.0 to 2.0 V at a scan rate of 50 mV s⁻¹ (solid line). At a negative potential of about -1.0 V (MMO), the formation of titanium hydride beside the oxide is possible. X-ray diffraction, scanning electron microprobe and Auger electron spectroscopy showed the presence of a duplicate oxide hydride film on Ti [34]. Our previous studies [35,36] showed the possibility of the formation of titanium oxides (Ti₂O₃ and TiO₂) from the surface layer of TiH₂ or Ti metal according to the following equations:



In the presence of 4.9 M methanol, the cyclic voltammetric behaviour of the Ti electrode is represented in Fig. 1a (dashed line) for the same potential window and at the same scan rate. The figure shows the presence of an anodic peak at about 1.30 V, probably due to methanol oxidation, the current density of which about 1.32 mA cm⁻² (this anodic peak did not appear at lower methanol concentrations). The current density value of this peak was found to decrease after the 5th cycle reaching finally a very low value, nearly zero current, upon further cycling (not presented in the figure). This could be attributed to the insulating effect of the oxide film, TiO₂ [33], which thickened during the oxidation of methanol at the oxide-covered Ti electrode. With repeated potential cycling, thickening of the TiO₂ takes place that prevents the further oxidation of methanol. However, Ti modified with Pt showed a much higher activity towards methanol oxidation as shown in Fig. 1b. In this experiment the electrode was prepared by potentiostatic deposition of Pt on Ti at -0.530 V (MMS) for 5 min. Hydrogen desorption experiment carried out for this electrode showed that the surface area is about 162.0 cm². Anodizing this electrode in NaOH solution at 50 mV s⁻¹ in the presence of 4.9 M methanol showed an oxidation peak at a much lower potential [about 0.20 V (MMO)] and has a current density value of about 40.0 mA cm⁻². This peak probably represents the electro-oxidation of methanol. Even

over potential cycling, the relative height of the oxidation peak for the first cycle and the 5th cycle in Fig. 1b is nearly the same. This indicates that not only the overpotential for methanol oxidation is lower than in case of Ti (Fig. 1a) but also the stability of the electrode over repeated cycling is improved by the presence of Pt deposits. Stability here means the preservation of the catalytic activity of the electrode.

The above results showed that, the catalytic oxidation of methanol on Pt/Ti electrode is much better than on bulk Ti alone or on bulk Pt. At the bulk Pt electrode (0.18 cm² surface area) (Fig. 2a), the methanol oxidation peak current density reached only a value of about 3.9 mA cm⁻². In this study, the polarization potential range was chosen to be restricted only in the range of methanol oxidation at the bulk Pt electrode; from -0.4 to 0.5 V (MMO). After 5 cycles in the methanol containing solution, the oxidation peak current density value reached about 72% of the first cycle. It is more convenient to compare the catalytic activity of platinum deposited on titanium with platinum deposited on platinum rather than with a massive platinum electrode. Fig. 2b represents the cyclic voltammograms recorded for Pt/Pt electrode. In this experiment Pt was deposited on Pt using the same experimental conditions as used for Pt/Ti electrode. Hydrogen desorption experiment carried out for this electrode showed that the real surface area is about 141.0 cm². Anodizing this electrode in NaOH solution at 50 mV s⁻¹ in the presence of 4.9 M methanol showed an oxidation peak at about 0.27 V (MMO) and has a current density value of about 25.0 mA cm⁻². This peak reached 80% of its current value after 5 cycles (Fig. 2b). Taking into consideration the real surface area of the two electrodes (Pt/Ti and Pt/Pt), one can find that the peak current density value of methanol oxidation at Pt/Ti electrode is 1.5 times greater than that at Pt/Pt electrode. It seems that there is no high difference between the current density values of methanol oxidation at the two modified electrodes. But with respect to stability over repeated potential cycling, it was found that Pt/Ti electrode is highly stable than Pt/Pt electrode as in case of the latter one the peak height reached 80% after 5 cycles. It is known that, the oxidation of methanol on bulk Pt electrodes occurs due to the presence of oxygenated species (PtO or PtOH), which help the oxidation of CO to CO₂ [37]. The methanol oxidation reaction requires the adsorption of methanol and the oxygen-containing species (e.g. OH_{ads}) on the substrate. Pt can adsorb and dehydrogenate methanol at relatively low potentials but it cannot adsorb OH at these potentials. It is therefore the objective of research on bimetallic catalysts to find a metal that can adsorb OH radical or any other oxygen-containing species at relatively lower potentials [37]. It was reported that [38], bonding of Pt to Ti produces a dramatic decrease in the density of states (DOS) near the Fermi level and an increase in the (DOS) near the bottom of d-band. An extended Huckel calculation of the Pt-Ti bonding showed that, these changes in (DOS) represent filling of the d-band by donation of d-electrons from Ti to unfilled Pt d-orbital. Ranjit et al. [39] and Kominami et al. [40] reported that noble metal-loaded catalysts (M/TiO₂) have been used in catalytic reaction because they have a high electron affinity. On the basis of these studies, it is expected to have a catalytic enhancement of Pt in the presence of Ti. On the bases of these discussions, it is suggested that the high catalytic activity of Pt/Ti electrode relative to that of the Pt/Pt one could be attributed to one of each of the following:

- the surface nature of Ti could facilitate the deposition of more Pt particles on its surface that resulted in increasing the real surface area of the electrode.
- in correlation with the report of Ranjit et al. [39] and Kominami et al. [40] and the extended Huckel calculation, Ti could increase the catalytic activity of Pt by its electrons donation to unfilled Pt d-orbital.

Fig. 3a and b shows the effect of changing the starting potential on methanol electro-oxidation in NaOH solution at bulk Ti and at Pt/Ti electrodes, respectively. As the polarization starts from more negative

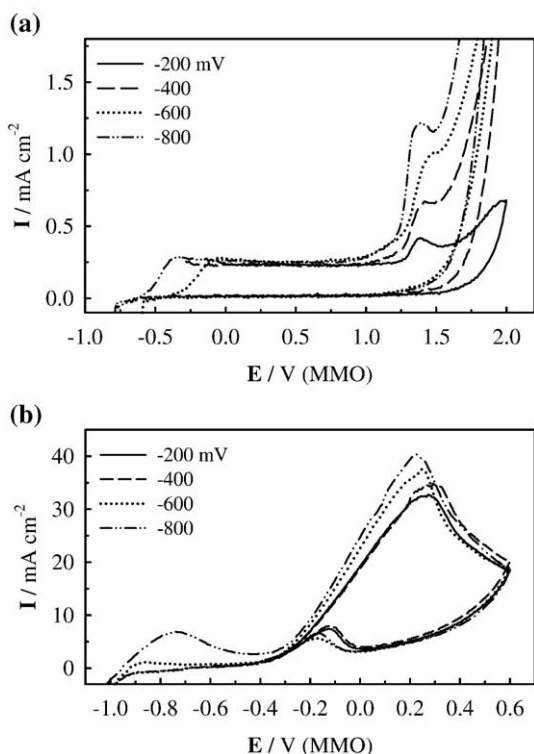


Fig. 3. Effect of changing the starting potential on methanol oxidation at (a) Ti electrode and (b) Pt/Ti electrode, in 0.5 M NaOH containing 4.9 M MeOH at a scan rate of 50 mV s^{-1} .

potentials, the oxidation peak current density of methanol at both electrodes increased and there was a slight shift in the peak potential, especially in case of the Pt/Ti electrode, towards less potential values. It is suggested from these results that, hydrogen evolution could have a great effect on the methanol electro-oxidation process. Several studies [41] reported that hydrogen can be incorporated into the metal either in the form of atomic hydrogen or becomes bound to the metal in the form of hydride. Part of the loaded hydrogen can diffuse into the oxide lattice and dissociates into electrons and protons. Accordingly, loading the metal with hydrogen may increase the conductivity of the electrochemically formed oxide by increasing the donor impurities and donating electrons to the conduction band [36]. Based on the above, the enhancement of methanol oxidation under the condition of polarizing the titanium or the platinum modified titanium electrode in the hydrogen evolution potential region could be due to one of the following or all:

- 1 – Activating the electrode surface through:
 - a) reducing titanium oxides and formation of a bare titanium surface, in case of the unmodified electrode (Ti), and
 - b) removing poisoning species from the surface of the modified electrode (Pt/Ti).
- 2 – The formation of Ti-hydride in this potential region could cause defects in the pre-formed oxide film and hence increasing the charge transfer reaction across it and accordingly increasing the number of active sites required for the adsorption of methanol and its oxidation products.
- 3 – It could possibly affect the distribution of Pt deposits at the Ti surface.

In another trial to understand the role of hydrogen loading in the methanol electro-oxidation process at Pt/Ti electrode, the effect of holding time in the hydrogen evolution potential region [-1.4 V versus MMO] was studied. The results are shown in Fig. 4 which represents the first and 50th cycles of voltammograms of the Pt/Ti electrode

during methanol electro-oxidation. The oxidation peak current density value was found to reach about 68% of its initial value after the 50 cycles. Because of the prolonged oxidation of methanol, the modified electrode could partially lose its catalytic activity as a result of the accumulation of methanol oxidation products leading to a decrease in the peak current density. Another possible explanation for the catalytic activity loss is the partial dissolution of Pt deposits and decreasing the number of active area responsible for methanol oxidation. After the 50th cycle, the potential of the working electrode was held at the potential region of hydrogen evolution for 5 min. This resulted in an increase in the peak current density and a shift of the peak potential to less positive values [dashed curve in Fig. 4]. Changing the holding time for various time intervals showed an increase in the peak current density and then it decreased again depending on the holding time [not represented in the figure]. At the potential of hydrogen evolution, -1.4 V , two processes were proposed: i) partial restoration of Pt active area upon reduction of the electrode could be due to redeposition of previously dissolved Pt, ii) activating the substrate, Ti, surface by reducing oxide thickness and thus facilitate the charge transfer process for the methanol oxidation process. Oxidation peak current density after the 50th cycles versus the first cycle is used here as an approximate way to access the stability of the electrode.

In an attempt to show the effect of Ti-hydride thickness on the methanol oxidation process, a mechanically polished Ti electrode was first polarized at the potential of hydrogen evolution (-1.4 V MMO) at different time intervals in 0.5 M NaOH. Different time intervals were used here as an indication of different hydride thickness [36]. The electrode, after each polarization experiment, was transferred into another cell containing the Pt deposition bath in which Pt was deposited potentiostatically for 5 min at -0.530 V (MMS). In each polarization experiment, at each time interval, a new pre-polished Ti electrode was used. After Pt deposition, the modified electrode was transferred into the electrolytic cell in which methanol oxidation was carried out. The same procedure was performed to study the effect of Ti-oxide thickness on the methanol oxidation process. In this case, the mechanically polished Ti electrode was pre-polarized potentiostatically at $+1.2 \text{ V}$ (MMO) in 0.5 M NaOH for different time intervals, also to have different oxide thickness. Each of the above experiments was

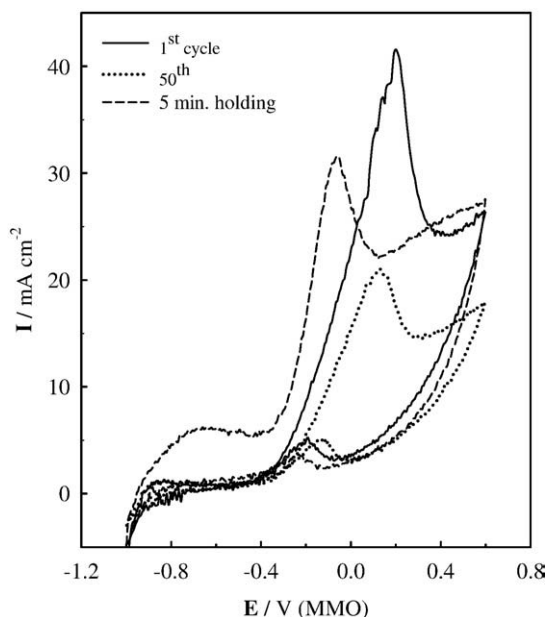


Fig. 4. Effect of the holding time at the hydrogen evolution potential region on the methanol oxidation process at Pt/Ti electrode in 0.5 M NaOH containing 4.9 M MeOH. (Scan rate is 50 mV s^{-1}).

Table 1
Variation of the amount of Pt deposits with the time of hydride and oxide formation

Amount of Pt deposited, mg cm ⁻²	Time for hydride formation, min					Time for oxide formation, min					
	5	10	15	20	25	1/2	1	2	5	10	15
	0.138	0.157	0.336	0.107	0.104	0.105	0.087	0.082	0.079	0.071	0.067

repeated several times in order to get a reproducible amount of Pt deposits at the same time interval. Table 1 represents the amount of Pt deposited in each case in mg cm⁻² at the different time intervals studied. In this case, the area used is the geometric area of the electrode (see the “Experimental techniques” section).

Fig. 5 represents the variation of the methanol oxidation peak current density values with the holding time at the hydrogen evolution potential (hydride thickening), Fig. 5a, and the time of oxide thickening, Fig. 5b. In Fig. 5a, it is clear that the methanol oxidation peak current density value increases up to a certain holding time after which it decreases again. The increase of methanol oxidation peak current density in the first 15 min holding time at the hydrogen evolution potential could be due to the increased amount of Pt deposits at the electrode surface (see Table 1). Increased amount of Pt deposits leads to a higher real surface area. As reported above, polarizing the Ti electrode at the hydrogen evolution potential region resulted in activating the electrode surface and reducing the pre-formed oxide, i.e., reaching a bare Ti surface. After 15 min polarization at the potential of hydrogen evolution the data in Table 1 shows a decreased amount of Pt deposits. The increased thickness of hydride layer could decrease the amount of Pt deposits as well as affect their distribution over the substrate surface and thus a decrease of the methanol oxidation peak current density was observed.

It is noticed in Fig. 5b that, as the Ti-oxide thickness increases the oxidation peak current density of methanol decreases. This is due to the decreased amount of Pt deposits (see Table 1). The results revealed that Ti-oxide has an inhibiting effect, at a relatively high thickness, for

methanol electro-oxidation. On one hand, Ti-oxide tends to create a non-reactive layer that cannot provide active oxygen to clean off the poisoning methanol oxidation products. On the other hand, it could not provide an effective surface area for Pt deposition so a decreased amount of Pt deposits was obtained as the oxide thickness increases. Another possibility is that thick Ti-oxide might restrict access of methanol to the Pt deposit.

Methanol oxidation was studied in 0.5 M NaOH at a scan rate of 50 mV s⁻¹ at the Pt/Ti modified electrode prepared by potentiostatic deposition technique for 5 min at -0.530 V (MMS) in the presence of various methanol concentrations. As the methanol concentration increases the peak current density of methanol oxidation increases up to 2.0 M methanol after which a decrease in the peak current density was observed (Fig. 6a). At higher methanol concentration, the rate of the electrode poisoning by oxidation intermediate products is increased, so a decrease in the oxidation peak current density was observed. Because 2.0 M methanol shows the highest current density value for methanol oxidation, it is used in the forgoing study. The order of reaction with respect to methanol was estimated from the logarithmic plot (Fig. 6a inset) of the peak current density versus the methanol concentration and was found to be 0.9. Some authors reported that values for the reaction order vary from zero (at low potential, high concentrations) to close to unity (at high potentials) at Pt/Ru catalyst [42]. On the other hand, at 2.0 M methanol, as the concentration of NaOH increases from 0.5 up to 3 M, the peak current density of methanol oxidation increases thereafter it decreased again at OH⁻ concentrations above 3.0 M (Fig. 6b). This means that, there is a

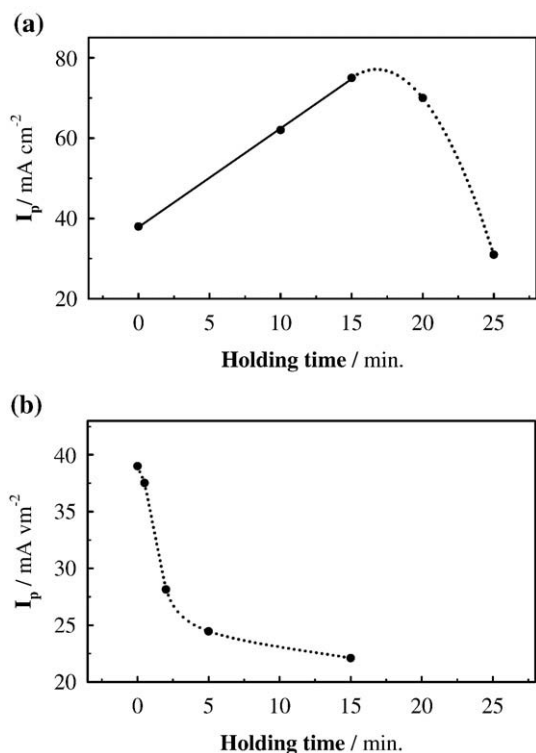


Fig. 5. Variation of the peak current density of methanol oxidation at the Pt/Ti electrode with the holding time (a) at the hydrogen evolution potential region (-1.4 V) and (b) at +1.2 V.

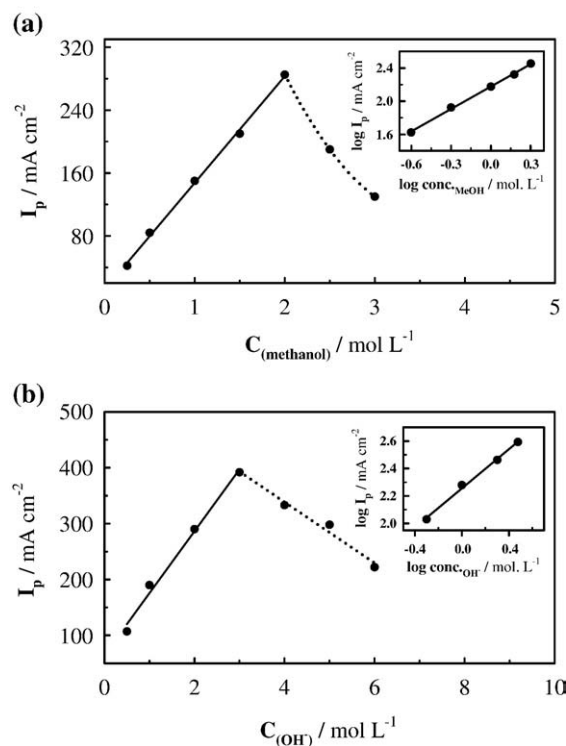


Fig. 6. Variation of the peak current density of methanol oxidation at the Pt/Ti electrode with: (a) methanol concentration, and (b) NaOH concentration. The logarithmic plots are presented in the inset.

Table 2
Variation of the real surface area of Pt deposits on Ti with the time of deposition

Time of Pt deposition (potentiostatically)	Real surface area (cm ²)	Time of Pt deposition (galvanostatically)	Real surface area (cm ²)
2	43	0.5	55
3	84	1	108
4	113	2	169
5	162	3	212
8	170	4	233
10	185	5	240
15	210	6	251
20	240		

certain ratio between the methanol and OH⁻ concentration at which the oxidation peak current density reaches its highest value. On the other hand, the decrease of methanol oxidation peak current density at relatively high OH⁻ concentrations could be due to the ionic strength effect. The order of reaction with respect to OH⁻ was estimated from the logarithmic plot (Fig. 6b inset) of the peak current density versus the NaOH concentration and was found to be 0.73. Yu et al. [18] reported a value for the reaction order with respect to OH⁻ ions close to 0.5 in the presence of methanol indicating that the adsorption of methanol and OH⁻ on the platinized Ti electrode follows Temkin isotherm. The same authors also reported that a poisoning effect was observed at MeOH/[OH⁻] concentration ratio greater than 1, which may be due to an excess of methanol and/or the depletion of OH⁻ ions at the electrode surface. In the present work and under the given experimental conditions, the MeOH/[OH⁻] concentration ratio that shows the highest methanol oxidation current density value is 0.67. It is clear that, OH⁻ ions have a great role in methanol electro-oxidation. It could be stated that, OH⁻ ions are a substrate in the rate determining step of the electrode process (electro-desorption of poisoning intermediates from Pt). In the above experiments, no changes in the catalytic activity due to different polarization histories would be expected as the electrode efficiency over repeated potential cycling is over 94.7%.

To investigate the effect of changing the amount of Pt deposited on a Ti electrode on the electro-oxidation of methanol, Pt was electro-deposited by potentiostatic technique at -0.530 V (MMS) at different time intervals. In another set of experiments, Pt was deposited galvanostatically at -1.0 mA at different time intervals. In both set of experiments, the real surface area of the modified electrodes was estimated using the hydrogen desorption method as described in the "Experimental techniques section". Data of the amount of charge consumed during hydrogen desorption on the modified electrodes and the calculated real surface area at the corresponding time of potentiostatic and galvanostatic deposition of Pt were tabulated in Table 2. Variation of the peak current density of methanol oxidation at the Pt/Ti electrode in 3.0 M NaOH in the presence of 2.0 M MeOH with the real surface area of Pt was represented in Fig. 7. Fig. 7a represents the relation for the potentiostatic Pt deposition while Fig. 7b for the galvanostatic deposition. In these cases, the current density values of methanol oxidation were calculated referring to the real surface area and not to the geometric area. It was found that, in both cases, as the real surface area increases the oxidation peak current density increases up to a certain area after which the oxidation peak current density of methanol either reaches almost a steady value (as in case of potentiostatic Pt deposition) or decreases (as in case of galvanostatic Pt deposition). The changes of the peak current density at a relatively high Pt content in both cases could be attributed to the relatively high surface coverage of Ti by Pt, i.e., reaching almost a saturation level.

A relatively higher oxidation peak current density values were obtained for methanol oxidation at electrodes prepared by galvanostatic Pt deposition. The difference between the catalytic activities of the modified electrode prepared by the different methods of deposition techniques could be due to the variation of the amount

and the real surface area of deposited Pt or to the arrangement of Pt deposits on the electrode surface.

The morphology and the spatial distribution of the deposited Pt particles on a Ti substrate were studied using the scanning electron microscopy (SEM) with operating voltage of 30 kV. Fig. 8 shows the SEM patterns of the bar Ti surface as well as of Pt deposited potentiostatically for 5.0 min and galvanostatically for 3.0 min. It is clear that, the Pt particles are almost uniformly spread in a condensed form on the Ti surface in case of the potentiostatic method (see Fig. 8b). In case of the galvanostatic deposition method (Fig. 8c), the Pt particles are spread in a more dispersed form with relatively smaller particle size. These changes in Pt-particle size and distribution on the Ti surface in the two methods of Pt deposition reflect why the galvanostatic deposition method produces higher oxidation peak current density than the potentiostatic one. Energy dispersive X-ray analysis (EDX) was used to characterize the surface composition and to correlate the results obtained from the two electrochemical deposition methods. The EDX patterns of the modified electrode demonstrate that the Pt percentage on the Ti surface is about 85.1% for the potentiostatic deposition method and 36.2% for the galvanostatic deposition one. Estimation of the true surface area of Pt deposited in both cases through measuring the hydrogen desorption shows that the surface area of Pt for both electrodes was 162.0 cm² and 212.3 cm² for the potentiostatic and galvanostatic deposition, respectively. These estimated values are in agreement with the results of EDX analysis as in case of galvanostatic Pt deposition technique the Pt particles are of smaller size and more dispersed on the Ti surface that exhibits higher surface area than in case of the potentiostatic Pt deposition one. Consequently, the peak current density values for methanol oxidation in case of the galvanostatic deposition method are almost higher than those obtained by the potentiostatic deposition due to the difference in the size of Pt particles and their distribution on the Ti substrate.

From the above study, it was found that the stability (preservation of catalytic activity) of Pt/Ti electrode over repeated cycling is much better than that of other electrodes (Ti, Pt, and Pt/Pt electrodes). In addition, the stability of the Pt/Ti modified electrode prepared by the galvanostatic Pt deposition was found to be relatively higher than that

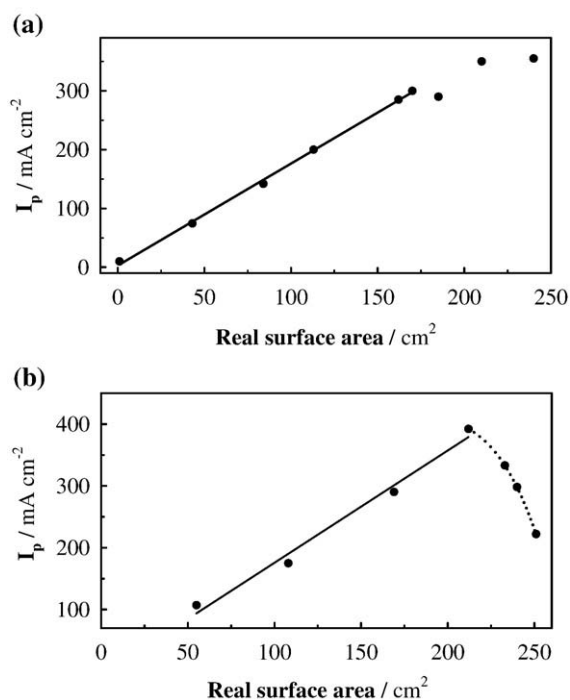


Fig. 7. Variation of the peak current density of methanol oxidation at the Pt/Ti electrode in 3.0 M NaOH+ 2.0 M MeOH with the real surface area of Pt: Pt deposited (a) potentiostatically at -0.530 V (MMS) and (b) galvanostatically at -1.0 mA.

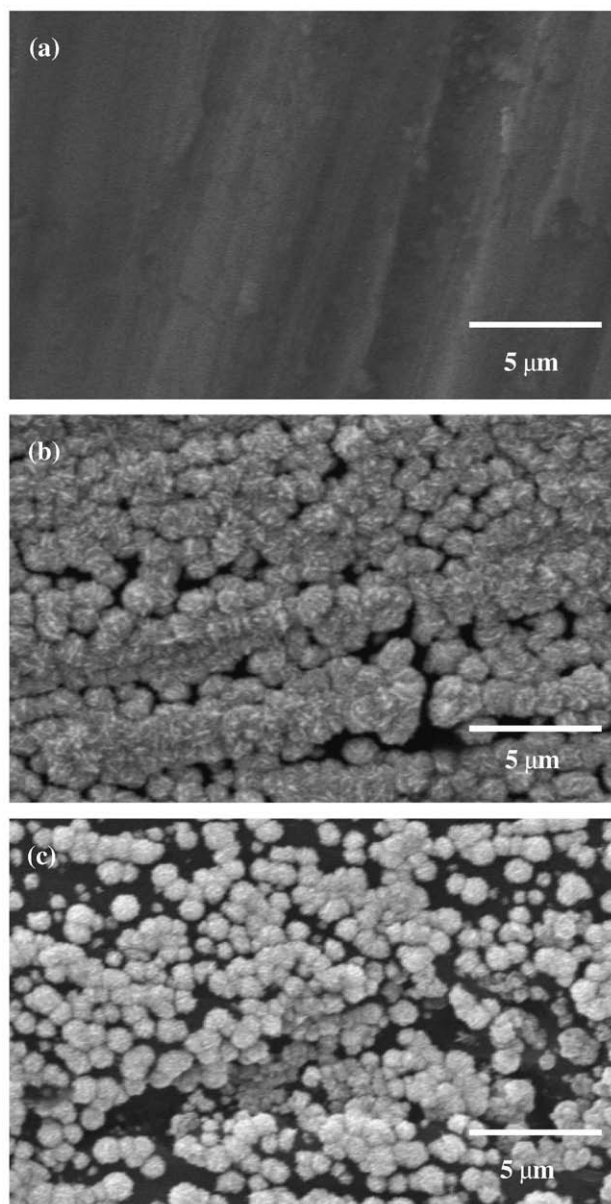


Fig. 8. Scanning electron micrographs of (a) mechanically polished Ti electrode, (b) Pt/Ti electrode after potentiostatic Pt deposition at -0.530 V (MMS) for 5.0 min and (c) Pt/Ti electrode after galvanostatic Pt deposition at -1.0 mA for 3.0 min.

prepared by the potentiostatic Pt deposition. Perhaps it could be due a better distribution of Pt deposits prepared by this technique at the Ti surface. The efficiency of Pt/Ti electrodes for methanol electro-oxidation after the 50th cycles reached 99.5% and 94.7% for the galvanostatic and potentiostatic Pt deposition, respectively, at methanol concentration of 2.0 M and 3.0 M NaOH at a scan rate of 50 mV s^{-1} . Efficiency here means the ability of the electrode to maintain its catalytic activity over repeated potential cycling in the test electrolyte. At higher methanol concentrations (up to 4.9 M), the value of the efficiency over repeated cycling decreased due to the rapid poisoning of the electrode by the intermediate products of methanol oxidation. The value of efficiency at this concentration is 83% and 68% for the galvanostatic and the potentiostatic Pt deposition, respectively.

Comparison was made between the chrono amperometric data of the Pt/Ti modified electrode with that of the Pt/Pt electrodes and of pure Pt and is presented in Fig. 9. The data was recorded by maintaining the electrode potential at a potential value corresponding to the methanol oxidation peak potential, 0.20 V (see Fig. 1b) and the

real surface area was considered in determining the current density values. In this experiment, the Pt/Ti and Pt/Pt modified electrodes were prepared by the galvanostatic Pt deposition at -1.0 mA for 3.0 min. Values of the estimated real surface area for the Pt/Ti, Pt/Pt and pure Pt electrodes are respectively 212.0, 171.0 and 45.7 cm^2 . The results of Fig. 9 show that, at an applied potential of 0.20 V, the Pt/Ti modified electrode delivers a relatively higher steady-state current density compared to Pt/Pt modified electrode and pure Pt. The current density measured for the Pt/Ti modified electrode is about 9.5 times greater than that for the Pt/Pt electrode and about 150 times greater than that for pure Pt electrode.

4. Conclusion

The electro-oxidation of methanol on a mechanically polished Ti electrode occurs at high overpotential. The process is inhibited with repeated cycling due to the thickening of the oxide film during methanol oxidation. Modification of Ti with Pt (Pt/Ti) has many advantages such as: a higher current density for methanol oxidation was obtained, a lower overpotential, a higher stability of the electrode over repeated cycling. The poisoning effect of the Pt/Ti modified electrode is less than in case of Pt/Pt or pure Pt, the removal of the poisoning species is much easier, and a faster rate for methanol electro-oxidation was observed. On the other hand, relatively higher oxidation peak current densities as well as better stability were obtained for the modified electrodes prepared by the galvanostatic Pt deposition technique than those prepared by the potentiostatic one due to the smaller Pt particle size and different distribution morphology. A comparison between the catalytic activity of Pt/Ti with that of Pt/Pt and pure Pt electrodes revealed that Pt/Ti is the relatively more efficient and more stable.

A considerable loss of the catalytic activity of the Pt/Ti electrode upon repeated cycling in the methanol-containing NaOH solution was observed. However, such electrode recovered most of its activity if it is polarized at the hydrogen evolution potential region for a definite time. It is believed that the polarization of the modified electrode at the potential of hydrogen evolution activates the electrode surface by partially reducing the pre-formed oxide and increasing the amount of Pt deposits over the electrode surface. Thick Ti-oxide and Ti-hydride (that could be formed during the electrode polarization in the hydrogen evolution potential region) retard the Pt deposition and accordingly affect the electro-oxidation of methanol. The order of the

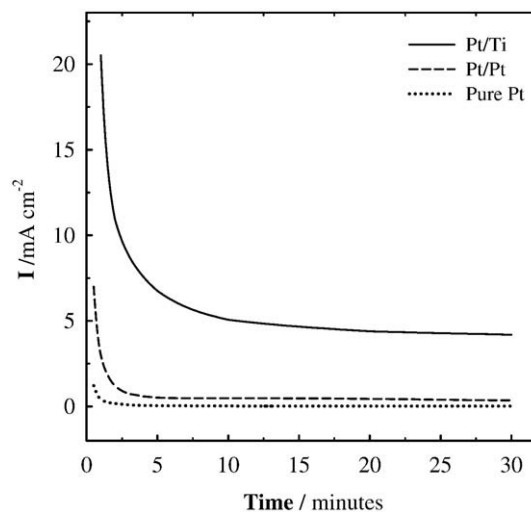


Fig. 9. Chrono amperometric measurements recorded at 200 mV (MMO) for Pt/Ti, Pt/Pt and pure Pt electrodes in 0.5 M NaOH solution containing 4.9 M MeOH. (Pt was deposited on Ti and Pt galvanostatically at -1.0 mA for 3 min).

reaction with respect to NaOH was found to be 0.73 and 0.9 with respect to methanol.

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