Pt Nanoparticles Supported on Tantalum: Preparation, Characterization and Application for Formic Acid Electro-oxidation

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ABSTRACT: Electrochemical characteristics of formic acid oxidation on a potent catalyst, platinum nanoparticles supported tantalum substrate (Pt-NPs/Ta) were investigated via cyclic voltammetric and chronoamperometric analysis in acidic solutions. The results were compared to those at a polycrystalline platinum electrode. It was found that Pt-NPs/Ta was catalytically more active than smooth platinum electrodes. The morphology and surface analysis of Pt-NPs/Ta catalysts were investigated using scanning electron microscopy and energy-dispersive X-ray spectroscopy, respectively. Finally, the long-term stability of Pt-NPs/T electrode has also been investigated. These results indicate that the system studied in the present work is the most promising system for use in fuel cells.

Key Words: Platinum nanoparticle, Electro-catalyst, Tantalum, Formic acid.

INTRODUCTION

Direct liquid fuel cells, such as direct methanol fuel cells (DMFCs) and direct formic acid fuel cells (DFAFCs), have attracted much attention in the past few decades due to their high energy conversion efficiency, low environmental pollution, and low operating temperature [1-3]. Recently the electrochemical oxidation of formic acid has been attracted more attention, because a direct formic acid fuel cell has some advantages over a direct methanol fuel cell. Formic acid is nontoxic, nonflammable and low crossover effect through the Nafion membrane because of anodic repulsion between the Nafion and the partially dissociated form of formic acid [4-7]. Pt has been extensively used for the electro-catalytic oxidation of formic acid [8-11]. It is now well-established that the electro-oxidation of formic acid to CO_2 on Pt electrodes proceeds via the so-called *dual-path mechanism* proposed originally by Capon and Parsons [12]. In this mechanism the direct path is normally a fast reaction involving an "active intermediate", while the second reaction proceeds via a "poisoning" intermediate, e.g., adsorbed carbon monoxide (CO_{ads}), which blocks the direct path. For the fuel oxidation on anodes and oxygen reduction on cathodes, highly active electro-catalysts are required to achieve the high enough current densities for practical applications. For a good electro-catalyst, both the high catalytic activity and the low cost must be considered to meet the final purpose of wide commercialization of fuel cells. In the previous studies, platinum was found to show the highest catalytic activity among the anode catalysts for electro-oxidation of formic acid. However, with platinum as an anode catalyst, the surface is usually heavily poisoned by the strong adsorption of CO produced during the oxidation of organic fuels, resulting in the lowering of catalytic performance. To resolve such a problem, many efforts have been devoted to reduce the poisoning effect by modifying Pt surface [3]. Modification of fuel cell anode with Pt and the binary Pt-Ru and Pt-Sn and the correlated ternary Pt-Ru-based and Pt-Sn-based catalysts has been proposed in several researches, but the high cost of Pt is not economic for industrial applications. Consequently some research activities have been done to find new and less expensive materials as anodes for DAFCs [13-17]. One of the ways to reduce the cost of fuel cell anodes is deposition of platinum nanoparticles on the less expensive materials such as aluminum, tungsten and titanium [18, 19]. To the best of our knowledge, up to now, there is not report on using tantalum

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as support for Pt nanoparticles in DFAFC. Tantalum has many outstanding properties such as chemical resistance (except to hydrofluoric acid), good conductivity, a high melting point, ductility, mechanical strength, and biocompatibility [20]. It is an important material for the construction of furnaces, chemical reactors, surgical instruments, capacitors, barrier layers in integrated circuits, and more [21, 22]. In the present work, for the first time, we prepared a high activity electro-catalyst based on the deposition of platinum nanoparticle (Pt-NP) on tantalum plate and studied their electrochemical activity for formic acid electro-oxidation using cyclic voltammetry.

EXPERIMENTAL

Solutions, chemicals and Equipment

Formic acid (Merck, 99% purity) and H_2SO_4 (Merck, 99% purity) were used as received. Hexachloroplatinic acid (98%) and sodium borohydride (98%) were purchased from Merck. All other chemicals were of analytical grade and used without further purification. All electrochemical experiments were carried out at room temperature. Distilled water was used throughout. The electrochemical experiments were performed in a three-electrode cell arrangement. A platinum sheet was used as counter electrode, while all potentials were measured with respect to a commercial saturated calomel reference electrode (SCE). Electrochemical experiments were carried out using a Compactstat Iviumstat, Model 2.175.

Preparation of Pt-NPs/Ta electrodes

Tantalum discs were cut from a tantalum plates (Alfa-Aesar, 99.95%) and mounted using polyester resin. The tantalum electrodes were first mechanically polished and then carefully rinsed, sequentially, in acetone, 2-propanol, and deionized water. The Pt-NPs were electrochemically deposited at the surface of tantalum substrate (Pt-NPs/Ta) from 1 mM H_2PtCl_6 in aqueous 0.5 M H_2SO_4 solution as the supporting electrolyte. The deposition conditions were a current density of 10 mA cm^{-2} for 10 min and the temperature is maintained at 45 °C.

Surface morphology of electrodes

For characterizing the morphology of Pt-NPs deposited on tantalum substrates, a scanning electron microscope (Model XL30, Philips, The Netherlands) was employed with an accelerating voltage 15 kV.

RESULTS AND DISCUSSION

Characterization of the electrodes morphology

Figure 1 shows Scanning electron microscopy (SEM) images of Pt-NPs deposited on the tantalum plate with different magnifications. As can be seen in this image, the platinum agglomerates with various sizes are formed and coverage of the surface is incomplete. Agglomerate is composed of a large number of Pt-NPs with diameters of 20-40 nm.
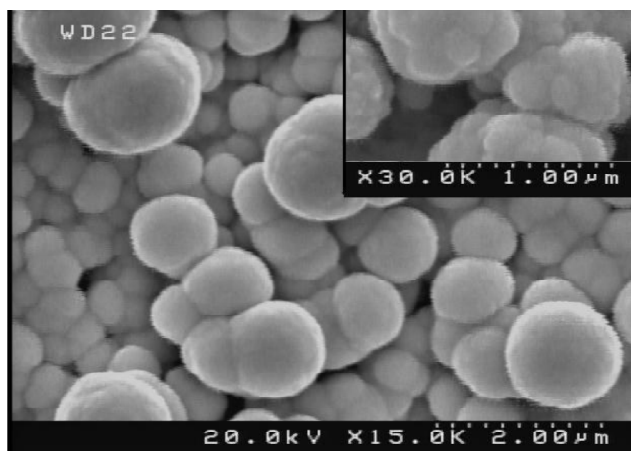

Figure 1:   The surface morphology of platinum nanoparticles deposited on the tantalum plate.

Characterization of the electrode surface and electrochemical behavior of Pt-NPs/Ta

To determine whether the deposition procedure by electrode-position method had resulted in the removal of the oxide layer, thereby ensuring good electrical contact between the platinum deposit and underlying tantalum electrode, the Pt-NPs/Ta were tested as electrodes using a one electron redox couple. Figure 2 shows the voltammetric curves for the reduction of $K_3Fe(CN)_6$ on Pt-NPs/Ta, smooth platinum and bare tantalum electrodes. The voltammogram for the Pt-NPs/Ta electrode shows the expected reversible behavior for the reduction on a bulk platinum electrode. It suggests that the adhesion and electrical contact of the platinum film with tantalum is quite satisfactory. In comparison, the voltammogram obtained with bare tantalum electrode shows increased peak separation and peak widths. This is probably attributable to a passivating surface
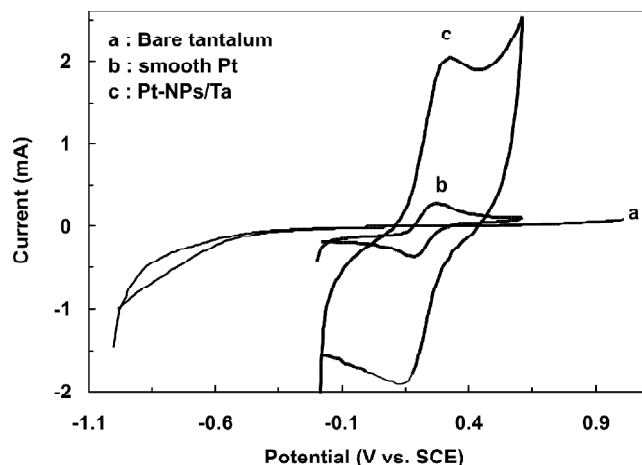
Figure 2: Cyclic voltammograms for Pt-NPs/Ta, smooth Pt and bare tantalum electrodes recorded solution containing 10 mM $K_3[Fe(CN)_6]$ in 1 M KCl at 25 °C with scan rate of 100 mV s^{-1}.

film, most likely the oxide layer present on the surface of the tantalum electrode [19].

To understand the electrochemical activity of the Pt-NPs/Ta, the cyclic voltammetric responses of the Pt-NPs/Ta, smooth platinum and bare tantalum electrodes were recorded at a scan rate of 100 mV s^{-1}. Figure 3 shows the cyclic voltammograms of the Pt-NPs/Ta, bare tantalum and smooth platinum (inset, curve a and b, respectively) in 0.5 M H_2SO_4 solution. Although the typical Pt-peaks for the hydrogen under-potential deposition (H_{upd}), the oxidation of hydrogen (H_{ox}), formation of platinum oxide (PtO_{for}), and its reduction (PtO_{red}) are present on the Pt-NPs/Ta, they become ill-shaped compared
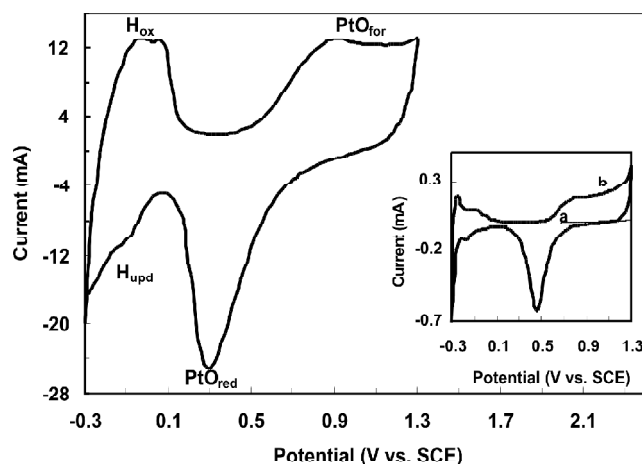

Figure 3: Cyclic voltammograms of Pt-NPs/Ta in 0.5 M H_2SO_4 at a scan rate of 100 mV s^{-1}. The inset is cyclic voltammograms of bare tantalum (curve a) and smooth Pt (curve b) in the same conditions.

to the smooth Pt (inset, curve b) [23, 24]. Curve b in inset of Fig. 3 shows the CV of bare tantalum substrate in 0.5 M H_2SO_4 solution. No adsorption/desorption peaks of hydrogen appeared at the bare tantalum.

The electro-catalytic oxidation of formic acid

In order to understand the electrochemical activity of the Pt-NPs/Ta, the cyclic voltammetric responses of the Pt-NPs/Ta and smooth platinum electrodes were recorded. Figure 4A presents cyclic voltammograms of smooth platinum electrode in 0.5 M H_2SO_4 aqueous solution, at a scan rate of 100 mV s^{-1} without formic acid (a) and at present 0.2 M formic acid (b). During the forward scan of the CV of smooth platinum electrode, the first anodic peak results from formic acid oxidation, while the second peak can be attributed to CO oxidation and formic acid oxidation on sites that were previously blocked by CO [25].

Cyclic voltammetry data were recorded for Pt-NPs/Ta electrode in 0.5 M H_2SO_4 aqueous solution, at a scan rate of 100 mV s^{-1} without formic acid (a) and at present 0.2 M formic acid (b) as shown in figure 4B. It can be seen from cyclic voltammogram of formic acid oxidation on the Pt-NPs/Ta electrode that the reaction commences in the hydrogen region and proceeds slowly in the positive direction, and then reaches a plateau at ca. -0.20 V. At potentials with more than ca. 0.10 V, the reaction becomes accelerated and maximum rate at ca. 0.85 V occurs. Upon reversing the potential sweep, a very steep increase of the reaction rate at ca. 0.54 V develops and a maximum current is observed at ca. 0.45 V. This large anodic peak in the reverse scan is attributed to the removal of the incompletely oxidized carbonaceous species formed in the forward scan [26]. Figure 4C shows the comparison of oxidation formic acid on smooth platinum electrode (a) and Pt-NPs/Ta electrode (b). It can be seen from figure 4C that cyclic voltammogram of Pt-NPs/Ta electrode shows the usual characteristics of smooth Pt electrode except that both for forward and reverse scan directions the oxidation currents of formic acid on the Pt-NPs/Ta electrode are significantly higher than on the smooth Pt electrode, indicating the surface area of Pt-NPs/Ta electrode was enlarged by dispersion platinum nanoparticles on tantalum substrate.
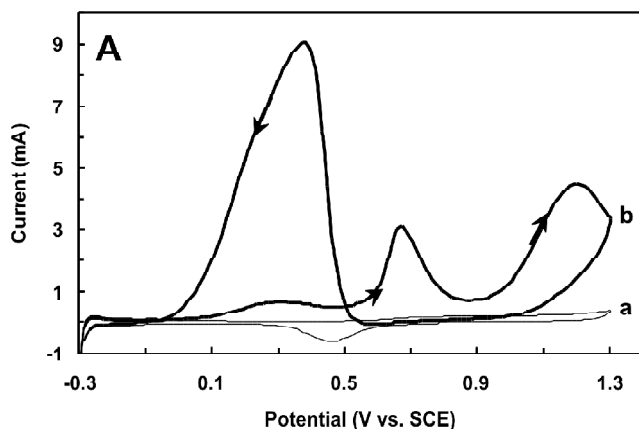
Figure 4: (A) The cyclic voltamogrames of smooth Pt electrode in 0.5 M H_2SO_4 without (a) and with (b) 0.2 M formic acid. (B) The cyclic voltamogrames of Pt-NPs/Ta electrode in 0.5 M H_2SO_4 without (a) and with (b) 0.2 M formic acid. (C) Cyclic voltammograms for smooth Pt electrode (a) and Pt-NPs/Ta electrode (b) in a 0.5 M H_2SO_4 + 0.2 M formic acid aqueous solution at 25 °C with a scan rate of 100 mV s^{-1}.

Parameters affecting the formic acid electro-oxidation

Effect of Scan Rate

The effect of different scan rates on the electro-catalytic properties of Pt-NPs/Ta electrode towards formic acid oxidation has been studied and results were shown in figure 5. As can be seen from figure 5, the increase in potential scan rate induced an increase in the electro-catalytic peak current and resulted in a shift to more positive potential value for the catalytic oxidation of formic acid. To find out the transport characteristics of Pt-NPs/Ta electrode, diagram of forward peak current i_{pf} versus square root of scan rate $\delta^{1/2}$ was constructed. As known in the precondition semi-infinite linear diffusion, anodic peak current i_p was related to scan rate through the following equation [27]:

$$i_p = (2.99 \times 10^5)\, n^{3/2}\, A\, C_o\, D_o^{1/2}\, \upsilon^{1/2}$$

Where:

i_p: anodic peak current

υ: scan rate

n: number of electrons transferred

C_o: bulk concentration of substrate

D_o: diffusion coefficient

A: the electrode surface area

If the concentration C_o is hold constant, the peak current i_p is linearly proportional to the square root of scan rate $\delta^{1/2}$. While the scan rate is kept constant, the peak current i_p is linearly proportional to the concentration C_o, which indicates the reaction is controlled by diffusion. It is seen from figure 5 (inset) that the peak current i_p is linearly related to the square root of scan rate $\upsilon^{1/2}$ and the correlation coefficient is $R^2 = 0.99$, which ensures that the oxidation process of formic acid on the Pt-NPs/Ta electrode is controlled by diffusion.
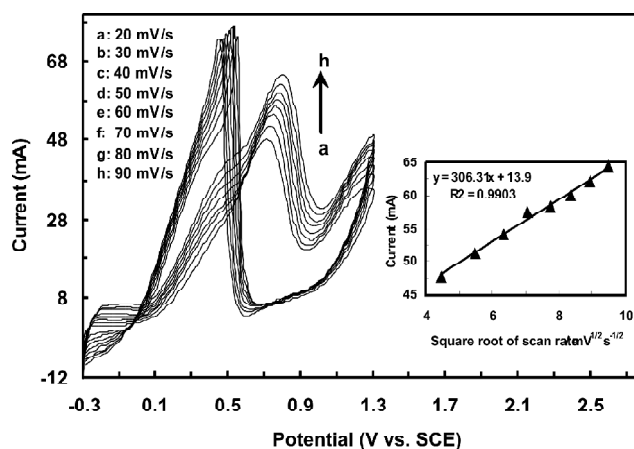

Figure 5: Cyclic voltammograms for Pt-NPs/Ta electrode in a 0.5 M H_2SO_4 + 0.2 M formic acid aqueous solution at 25°C at different scan rates: (Inset) Dependence of formic acid (forward) oxidation peak current on the square root of scan rates.

Effect of upper limit potentials region on the electro-oxidation of formic acid

Figure 6 shows cyclic voltammograms of formic acid oxidation on Pt-NPs/Ta for different final potential scan limit. As can be seen in Fig. 6, extending the anodic potential limit to the positive direction in forward scan caused a significant decrease in the current of re-oxidation peak in backward scan. Extending the potential window to the positive direction in forward scan accelerates the formation of oxide species (e.g., platinum oxides) and causes a decrease in the re-oxidation peak current [28, 29]. Also, by increasing the forward potential scan limit, re-oxidation peak potential shifts negatively because of stabilizing of oxidative platinum surfaces in high potentials and difficult reduction of them in backward scan.
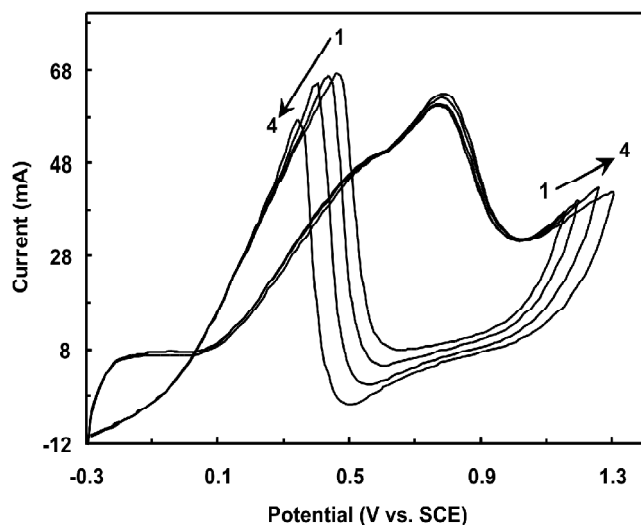
Figure 6: Effect of upper limit of potential scanning region on the electro-oxidation of 0.2 M formic acid on the Pt-NPs/Ta electrode in 0.5 M H_2SO_4 from (a) - 0.3 V-1.15 V to (f) -0.3 V-1.30 V with a scan rate of 100 mV s^{-1}.

Effect of formic acid and electrolyte concentration

In order to evaluate the capacity of Pt-NPs/Ta for electro-oxidation of formic acid, the effect of formic acid concentration on the corresponding main anodic peak currents was investigated by cyclic voltammetry and results show that the peak current of formic acid was increased by formic acid concentration, and reached a nearly constant value for concentrations higher than 1 M formic acid. We assume this effect caused by saturation of active sites at the surface of electro-catalyst.

In addition, the effect of H_2SO_4 concentration on the peak current related to the electro-oxidation of formic acid at Pt-NPs/Ta electrode has been investigated by CV. The variation of peak current of formic acid oxidation was plotted against H_2SO_4 concentration. The peak current of formic acid oxidation increased with the increase of H_2SO_4 concentration to 0.2 M. Further increase in H_2SO_4 concentration depressed the anodic peak current. It can be said that in high concentrations of H_2SO_4, the dissociation of acid decreases and causes the solution conductivity to be reduced. Also, the reducing effect of high level H_2SO_4 concentration on peak currents may be addressed according to the Chatelier's principle, i.e. the thermodynamic tendency for oxidation of formic acid was reduced by H_2SO_4 concentration [23].

Effect of deposition time

According to the available literature, the electrochemical catalytic activity of platinum particles strongly depends on the deposited mass of platinum. In this work, the effect of different deposition time from 1 min to 15 min of platinum electrodeposition on the tantalum surface on the oxidation of formic acid was studied. The CVs obtained in 0.2 M H_2SO_4 + 0.5 M formic acid at scan rate of 100 mV s^{-1} were driven and the variation of anodic peak currents for formic acid vs. the deposition time were plotted. Results show that the anodic peak currents of formic acid increases with an increase in the deposition time from 1 min to 10 min and then remain constant for the optimum platinum amount of 9-11 min. The anodic peak currents obtained for formic acid oxidation decrease with an increase in the deposition time to 15 min. In the interpretation of this phenomenon can be said that for platinum loadings above 9-11 min, the accumulation of platinum occurs; in other words, at the lower platinum depositions, metal particles are almost uniformly deposited on the surface of tantalum substrate and the real area of platinum particles increases that causes an enhancement in the electro-catalytic activity of Pt-NPs/Ta electrode. When the platinum loading further increased, the metal particles agglomerate during the reduction process and result in the decrease of the electrochemical active area.

Chronoamperometric study of oxidation of formic acid on Pt-NPs/Ta electrode

In order to evaluate the electro-catalytic performance of the Pt-NPs/Ta for formic acid oxidation under long-term operation condition, chronoamperometric (CA) measurements were carried out by applying different potential steps inside the formic acid oxidation potential region (0.0, 0.2, 0.4, 0.6 and 0.9V vs. SCE) for 500 s. Figure 7 shows the chronoamperometric curves for the Pt-NPs/Ta in 0.5 M H_2SO_4 +0.2 M formic acid at different potential steps. As can be seen, in all CA curves the currents dropped rapidly at first, which can be explained by fast surface poisoning by adsorbed intermediates [30, 31], and then became relatively stable. The initial high current corresponds mainly to double layer charging. As shown in Fig. 7, for step potential of 0.9 V the current of plateau is the most one, because this potential is close to the potential of anodic peak in

the cyclic voltammograms. Inset of figure 7 shows typical chronoamperogram curve carried out in different potential steps inside the formic acid oxidation potential region (0.35 and 0.70 V vs. SCE) for 500 s on smooth platinum electrode. The rapid current decay shows the poisoning of Pt electrode.
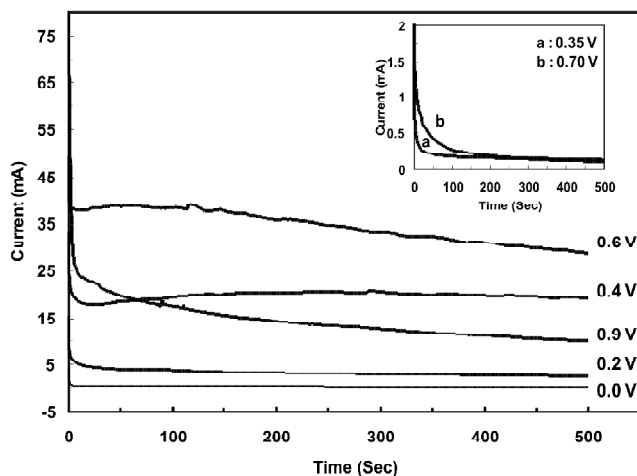

Figure 7: Chronoamperometric curves obtained on the Pt-NPs/Ta electrode in 0.5 M H_2SO_4 + 0.2 M formic acid aqueous solution for different potential steps. The inset is Chronoamperometric curves obtained on the smooth Pt electrode in the same solution for different potential steps.

CONCLUSION

For preparation of a low cost electro-catalyst for formic acid oxidation, Pt-NPs/Ta electrodes were prepared by electro-deposition of Pt nanoparticles on tantalum plates. The resulting sample structures provide high surface area. The electro-activity of these catalysts for formic acid oxidation was studied using electrochemical techniques. The catalysts exhibited much higher activity for formic acid electro-oxidation than the smooth platinum. This can be attributed essentially to the large real surface area of the catalyst particle and/or the catalyst particles are probably less sensitive to poisoning from adsorbed species. The prepared electrodes exhibit satisfactory stability and reproducibility when stored in ambient conditions, which could be a good choice for the formic acid oxidation in the promising formic acid fuel cell.

References

[1]   Dillon R, Srinivasan S, Arico A S, Antonucci V, International activities in DMFC R&D: status of technologies and potential applications, *J Power Sources*. 127, **2004**, 112-126.

[2]   Lamy C, Lima A, LeRhun V, Delime F, Coutanceau C, Leger JM, Recent advances in the development of direct alcohol fuel cells (DAFC), *J Power Sources*. 105, **2002**, 283-296.

[3]   Lu Y, Chen W, Nanoneedle-covered Pd-Ag nanotubes: high electrocatalytic activity for formic acid oxidation, *J. Phys. Chem. C*. 114, **2010**, 21190-21200.

[4]   Zhu Y M, Khan Z, Masel R I, The behavior of palladium catalysts in direct formic acid fuel cells, *J. Power Sources*. 139, **2005**, 15-20.

[5]   Rice C, Ha S, Masel R I, Wieckowski A, Catalysts for direct formic acid fuel cells, *J Power Sources*. 115, **2003**, 229-235.

[6]   Rhee Y W, Ha S Y, Masel R I, Crossover of formic acid through Nafion membranes, *J Power Sources*. 117, **2003**, 35-38.

[7]   Liu Y, Wang L, Wang G, Deng C, Wu B, Gao Y, High Active Carbon Supported PdAu Catalyst for Formic Acid Electro-oxidation and Study of the Kinetics, *J Phys Chem C*. 114, **2010**, 21417-21422.

[8]   Uhm S, Kwon Y, Chung S T, Lee J, Highly effective anode structure in a direct formic acid fuel cell, *Electrochim Acta*. 53, **2008**, 5162-5168.

[9]   Lu G Q, Crown A, Wieckowski A, Formic acid decomposition on polycrystalline platinum and palladium electrodes, *J Phys Chem B*. 103, **1999**, 9700-9711.

[10] Ren F F, Zhou W Q, Du Y, Yang P, Wang C, Xu J K, High efficient electro-catalytic oxidation of formic acid at Pt dispersed on porous poly(o-methoxyaniline), *Int J Hydrogen Energy*. 36, **2011**, 6414-6421.

[11] Selvaraj V, Alagar M, Kumar K S, Synthesis and characterization of metal nanoparticles-decorated PPY-CNT composite and their electro-catalytic oxidation of formic acid and formaldehyde for fuel cell applications, *Appl Catal B Environ*. 75, **2007**, 129-138.

[12] Capon A, Parsons R, The oxidation of formic acid on noble metal electrodes II. A comparison of the behavior of pure electrodes, *J Electroanal Chem*. 44, **1973**, 239-254.

[13] Ribeiro J, dos Anjos D M, Kokoh K B, Coutanceau C, Léger J M, Olivi P, de Andrade A R, Tremiliosi-Filho G, Carbon-supported ternary PtSnIr catalysts for direct ethanol fuel cell, *Electrochim Acta*. 52, **2007**, 6997-7006.

[14] Wang Z B, Yin G P, Lin Y G, Synthesis and characterization of PtRuMo/C nanoparticle electro-catalyst for direct ethanol fuel cell, *J Power Sources*. 170, **2007**, 242-250

[15] Li H, Sun G, Cao L, Jiang L, Xin Q, Comparison of different promotion effect of PtRu/C and PtSn/C electro-catalysts for ethanol electro-oxidation, *Electrochim Acta*. 52, **2007**, 6622-6629.

[16] Witham C K, Chun W, Valdez T I, Narayanan S R, Performance of direct methanol fuel cells with sputter-deposited anode catalyst layer, *Electrochem Solid State Lett*. 3, **2000**, 497-500.

[17] Razmi H, Habibi Es, Heidari H, Electro-catalytic oxidation of methanol and ethanol at carbon ceramic electrode modified with platinum nanoparticles, *Electrochim Acta.* 53, **2008**, 8178-8185.

[18] Pournaghi-Azar M H, Habibi B, Preparation of a platinum layer modified aluminum electrode by electrochemical and electroless cementations and its use for the electrooxidation of methanol, *J Electroanal Chem.* 580, **2005**, 23-34.

[19] Hosseini M G, Sajjadi S A S, Momeni M M, Electro-deposition of platinum metal on titanium and anodized titanium from P salt: application to electro-oxidation of glycerol, *Surf Eng.* 23, **2007**, 419-424.

[20] Findlay D M, Welldon K, Atkins G J, Howie D W, Zannettino A C W, Bobyn D, The proliferation and phenotypic expression of human osteoblasts on tantalum metal, *Biomater.* 25, **2004**, 2215-2227.

[21] Chaneliere C, Autran J L, Devine R A B, Balland B, Tantalum pentoxide (Ta_2O_5) thin films for advanced dielectric applications, *Mater Sci Eng R.* 22, **1998**, 269-322.

[22] Kuiry S C, Seal S, Fei W, Ramsdell J, Desai V H, Li Y, Babu S V, Wood B, Effect of pH and H_2O_2 on Ta chemical mechanical planarization, *J Electrochem Soc.* 150, **2003**, C36-C43.

[23] Habibi B, Delnavaz N, Electro-catalytic oxidation of formic acid and formaldehyde on platinum nanoparticles decorated carbon-ceramic substrate, *Int J Hydrogen Energy.* 35, **2010**, 8831-8840.

[24] Razmi H, Es Habibi, Heidari H, Electro-catalytic oxidation of methanol and ethanol at carbon ceramic electrode modified with platinum nanoparticles, *Electrochim Acta.* 53, **2008**, 8178-8185.

[25] Jayashree R S, Spendelow J S, Yeom J, Rastogi C, Shannon M A, Kenis P J A, Electro-oxidation of formic acid on electrodeposited Pt and Pt/Pd catalyst structures, *Electrochim Acta.* 50, **2005**, 4674-4682.

[26] Zhang L, Wang Z, Xia D, Bimetallic PtPb for formic acid electro-oxidation, *J Alloys Compd.* 426, **2006**, 268-271.

[27] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamental and Applications, John Wiley & Sons, New York, 1980.

[28] Manohara R, Goodenough J B, Methanol oxidation in acid on ordered NiTi, *J Mater Chem.* 2, **1992**, 875-887.

[29] Hosseini M G, Momeni M M, Evaluation of the performance of platinum nanoparticle-titanium oxide nanotubes as a new refreshable electrode for formic acid electro-oxidation, *Fuel Cells.* 12, **2012**, 406-414.

[30] Rightmire R A, Rowland R L, Boos D L, Beals D L, Ethyl alcohol oxidation at platinum electrodes, *J Electrochem Soc.* 111, **1964**, 242-247.

[31] Iwasita T, Pastor E, A DEMS and FTIR spectroscopy investigation of adsorbed ethanol on polycrystalline platinum, *Electrochim Acta.* 39, **1994**, 531-537.