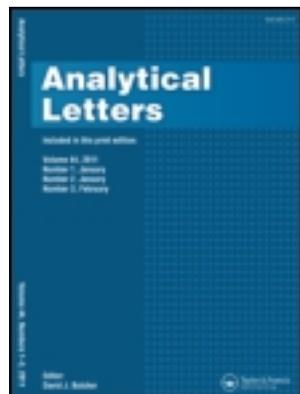


This article was downloaded by: [University of Lethbridge]

On: 09 January 2014, At: 05:11

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Analytical Letters

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lanl20>

A Glassy Carbon Electrode Modified by Polypyrrole and Platinum Nanoparticles to Enhance the Catalytic Oxidation of Methanol

Iman Razavipanah^a, Gholam Hossein Rounaghi^a & Mohammad Hossein Arbab Zavvar^a

^a Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

Accepted author version posted online: 26 Nov 2013. Published online: 27 Dec 2013.

To cite this article: Iman Razavipanah, Gholam Hossein Rounaghi & Mohammad Hossein Arbab Zavvar (2014) A Glassy Carbon Electrode Modified by Polypyrrole and Platinum Nanoparticles to Enhance the Catalytic Oxidation of Methanol, *Analytical Letters*, 47:1, 117-133, DOI: [10.1080/00032719.2013.832277](https://doi.org/10.1080/00032719.2013.832277)

To link to this article: <http://dx.doi.org/10.1080/00032719.2013.832277>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Electrochemistry

A GLASSY CARBON ELECTRODE MODIFIED BY POLYPYRROLE AND PLATINUM NANOPARTICLES TO ENHANCE THE CATALYTIC OXIDATION OF METHANOL

Iman Razavipanah, Gholam Hossein Rounaghi, and
Mohammad Hossein Arbab Zavvar

*Department of Chemistry, Faculty of Sciences, Ferdowsi University of
Mashhad, Mashhad, Iran*

A nanocomposite surface coating was prepared by electropolymerization of pyrrole by cycling the electrode potential between -0.8 and 0.8 V (vs. SCE) on the surface of a glassy carbon electrode (GCE). After formation of the polypyrrole (PPy) matrix, this surface was potentiostatically coated with platinum nanoparticles at constant potential of -0.2 V (vs. SCE). The resulting electrode is referred to as GCE/PPy/Pt. The microscopic structure and morphology of the PPy film were characterized by scanning electron microscopy. The platinum nanoparticles were uniformly dispersed in the PPy matrix, as confirmed by transmission electron microscopy. The electrochemical and catalytic activities of the GCE/PPy/Pt were compared with GCE/Pt in $0.3 \text{ mol L}^{-1} \text{ HClO}_4$ solution. The electrooxidation of methanol on the GCE/PPy/Pt was studied by means of electrochemical techniques. The modified electrode exhibited a significant electrocatalytic activity for methanol oxidation compared to the other electrodes used in this study. The kinetics of methanol oxidation on GCE/PPy/Pt were studied.

Keywords: Electrocatalyst; Kinetic study; Methanol electrooxidation; Platinum nanoparticle; Polypyrrole

INTRODUCTION

In recent decades, due to high energy demands, fossil fuel depletion, and environmental pollution throughout the world (H. Liu et al. 2006), there has been an increasing interest in the development of fuel cells, because they can directly convert chemical energy to electrical energy with higher efficiency than other sources of electrical power (Yano, Shiraga, and Kitani 2008). Among fuel cells, the direct methanol fuel cell (DMFC) is one of the most attractive ones because of high energy conversion efficiency and low environmental intrusion and without a reformer

Received 13 May 2013; accepted 15 July 2013.

The authors gratefully acknowledge the support of this work by Ferdowsi University of Mashhad, Mashhad, Iran.

Address correspondence to Gholam Hossein Rounaghi, Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran. E-mail: ghrounaghi@yahoo.com; ronaghi@um.ac.ir

(Wasmus and Kuver 1999). Among the numerous materials for electrocatalytic oxidation of methanol, platinum has been established as a powerful electrocatalyst for this reason (Parsons and Van der Noot 1988). But the use of platinum in the form of smooth foils for the direct electrooxidation of methanol is found to be inefficient, first due to the high cost and secondly because of formation of strongly adsorbed intermediates like CO as a result of dissociative adsorption of methanol (Beden et al. 1987). Many attempts have, therefore, been made to overcome these problems and to develop less expensive anode materials, which have significantly better catalytic activity and are less prone to CO poisoning. These include the use of bimetallic catalysts such as Pt–Ru (Saffarian et al. 1998; L. Liu et al. 1998), Pt–WO₃ (Shen and Tseung 1994) and alloys of Ru–Pd (He, Kunz, and Fenton 1997) that reduce the overpotential for methanol oxidation considerably but are not cost effective. Among these attempts, using conducting polymers as support for platinum catalyst particles for the anodic oxidation of hydrogen or small organic molecules has been the subject of numerous investigations (Habibi et al. 2008; C. C. Chen, Bose, and Rajeshwar 1993; Del Valle et al. 1998; Kelaidopoulou et al. 1998; Kulesza et al. 1999).

Conducting polymers can effectively solve the aforementioned problems. First of all, because dispersing metallic particles inside these polymers give electrodes with higher surface areas leading to extraordinary electrocatalytic activities towards the oxidation of methanol molecules (Pournaghi–Azar and Habibi 2007a) and reduce the cost of electrodes materials. Secondly, the conducting polymers cause the higher tolerance of the platinum particles to poisoning due to the adsorption of CO species, in comparison with the bulk platinum electrodes (Selvaraj, Alagar, and Hamerton 2006). The conducting polymers used are mainly polyaniline (Niu et al. 2005; Niu et al. 2003a; Rajendra Prasad and Munichandraiah 2002; Cai and Chen 1998; Niu et al. 2003b; Mikhaylova et al. 2001; Castro Luna 2000; Hable and Wrighton 1993; Kessler and Castro Luna 2002), polythiophene (Biallozor, Kupniewska, and Jasulaitene 2003; Yassar, Roncali, and Garnier 1988; Swathirajan and Mikhail 1992), and polypyrrole (Bouzek, Mangold, and Jüttner 2001; Hammache, Makhoulfi, and Saidani 2001). Among them, conducting polypyrrole has been the focus of a great deal of research for catalytic materials in recent years because its superior properties that include high electric conductivity, high specific capacitance (easy up to 100 F g⁻¹), and good chemical and thermal stability, especially facile synthesis, and environmentally friendly (Zhao et al. 2010).

In the present work, we describe the development of a polypyrrole/platinum nanocomposite (PPy/Pt) surface coating on a glassy carbon electrode (GCE). Nanocomposites of metal-polymers or metal oxide-polymers are expected to be an important class of materials in the area of nanotechnology (Mulligan et al. 2001). These novel materials possess electronic and optical properties, which are distinctly different from those of individual nanoparticles. The electrocatalytic activity of PPy/Pt coated GCE toward the methanol oxidation is compared with other modified electrodes such as GC/Pt and Pt/Pt by means of different electrochemical studies. The use of conducting polymers as supporting matrices for the immobilization of nanomaterials for electrocatalytic purposes has been the subject of few studies, but as there are not a lot of studies on the kinetic analyses of the electrooxidation of alcohols, this investigation was carried out from the kinetic studies point of view. In addition, to the author's knowledge, the investigation of PPy/Pt nanocomposite

from the kinetic studies point of view has not yet been reported. Furthermore, studies of electrochemical characterization of the GCE/PPy/Pt and calculation of real surface area of this electrode also have not yet been reported.

EXPERIMENTAL

Chemicals

Pyrrrole was purchased from Merck and purified by distillation and refrigerated until use. LiClO_4 was purchased from Acros. Methanol, H_2PtCl_6 , and HClO_4 were purchased from Merck. All the solutions were prepared with double-distilled water. High purity nitrogen (99.999%, Sabalan Gas Company, Iran) was used for deaeration of the solutions.

Instrumentation

The electrochemical experiments were carried out using a potentiostat/galvanostat (μ Autolab Type III). A conventional three electrode cell was used at room temperature. A glassy carbon electrode (with a diameter of 2 mm, obtained from Azar Electrode Co., Urmia, Iran), bare or modified according to the case, was used as the working electrode. A saturated calomel electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2$, KCl 3 M) and a platinum wire were used as the reference and auxiliary electrodes, respectively. Morphological scanning electron microscope (SEM) images were obtained using a Hitachi S4160 field emission scanning electron microscope (Japan). Transmission electron microscope (TEM) images were obtained with a LEO-912 AB transmission electron microscope (Germany). Surface elemental analysis of electrodes was performed by the energy dispersive X-ray (EDX) technique using Oxford-7353 EDX microanalyzer. Infrared spectroscopy (Thermonicolet-Avatar-370) was employed to verify the synthesis of PPy film.

Preparation of GCE/PPy/Pt

The glassy carbon electrode (GCE) surface was polished with a slurry of 0.5 μm alumina. The polished surface was then rinsed with double-distilled water and sonicated in water-ethanol mixture for 5 min. Electropolymerization of pyrrole at the GCE was achieved by a potentiodynamic method. The electrode was immersed in an aqueous solution of 0.03 mol L^{-1} LiClO_4 containing 0.01 mol L^{-1} pyrrole. The electropolymerization was carried out by cycling the electrode potential between -0.8 and 0.8 V vs. SCE at scan rate of 50 mVs^{-1} . The thickness of deposited film (d_n) at the surface of GCE was calculated from the charge consumed (Q_a) during the electrodeposition of PPy film (the overall charge that passed during the anodic sweeps of potential) using Faraday's law, assuming a two electron mechanism based on the monomer molecule implied in the process; the current efficiency is 100%; a PPy density (ρ) of 1.5 g ml^{-1} , and a pyrrole molar mass (M) of 67 g mol^{-1} (Beck et al. 1994; Kanazawa et al. 1979).

$$d_n = Q_a/nF\rho \quad (1)$$

The electrodeposition of platinum was carried out in 0.2 mol L⁻¹ HClO₄ containing 0.002 mol L⁻¹ H₂PtCl₆ solutions using constant potential at the surface of GCE/PPy. Electrodeposition of Pt was performed potentiostatically at -0.2 V vs. SCE. The amount of Pt was evaluated from the quantity of charge (Q_{dep}) used during the electrodeposition process at -0.2 V. Q_{dep} was calculated from the integral of I/t transient response. As the partial reduction of PtCl₆²⁻ to Pt²⁺ species should occur at potentials more positive than 0.11 V and as the hydrogen evolution or charging of the conducting film were negligible at -0.2 V (Shimazu, Weisshaar, and Kuwana 1987), a current efficiency close to 100% was expected (Habibi et al. 2009). Thus, Q_{dep} (mC cm⁻²) resulting from the PtCl₆²⁻ total reduction was used for the evolution of deposited Pt. The Pt loading (W in mg cm⁻²) is then:

$$W = Q_{\text{dep}}M/zF \quad (2)$$

where M = 195.078 g mol⁻¹ is the atomic weight of Pt, z = 4 the number of exchanged electrons, and F = 96500 C mol⁻¹, the faradic constant.

For comparison, the PPy/Pt nanocomposite was synthesized under the same conditions at the surface of platinum electrode. This electrode was referred to as Pt/PPy/Pt. In addition, GCE/Pt was also synthesized under the same conditions without carrying out the electropolymerization stage.

RESULTS AND DISCUSSION

Mechanism of Electrochemical Polymerization of Pyrrole

PPy can be formed electrochemically through oxidative polymerization of the pyrrole monomer. Electrochemical oxidation of pyrrole forms a film of conducting polymer at the electrode surface. The electropolymerization of pyrrole to polypyrrole proceeds as follows (Scheme 1):

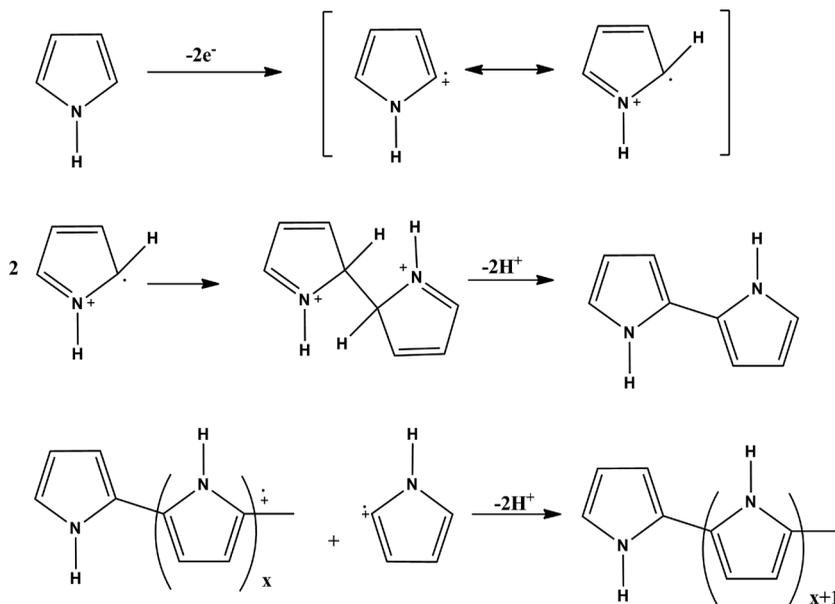
Initiation. Formation of monomer radical cation by cycling the electrode potential between -0.8 and 0.8 V (vs. SCE).

Propagation. Combination of two radical cation monomers (or oligomers) followed by loss of two hydrogen ions.

Termination. Occurs when no further monomer is present for oxidative polymerization or side reactions terminate the PPy chain. An example of a termination reaction is the reaction with water to form the amide group.

Infrared Characterization of PPy Film

In order to confirm the synthesis of PPy film, an infrared spectrum of the PPy film was obtained. Figure 1a shows the spectrum of pure PPy. The bands at 1546 (2,5-substituted pyrrole) and 1453 cm⁻¹ were assigned to typical PPy ring vibrations. The bands at 1312 and 1039 cm⁻¹ may correspond to =C-H band in plane vibration (Vishnuvardhan et al. 2006). The peak observed at 889 cm⁻¹ may be assigned to the =C-H out of plane vibration indicating polymerization of pyrrole (W. Chen



Scheme 1. Mechanism of electrochemical polymerization of pyrrole.

et al. 2003). Figure 1b shows the spectrum of pure pyrrole that was given for comparison.

SEM, TEM, and EDX Analysis of PPy/Pt Composite

The electron microscopic (EM) images of synthesized conducting PPy and PPy/Pt composites on GCE are shown in Figs. 1c and 1d, respectively. Figure 1c shows scanning electron microscopy (SEM) images of the unmodified PPy film with a uniform coverage and lumpy morphology formed on the surface of GCE. The size and morphology of the synthesized platinum particles, as well as their dispersion in the PPy film, were determined with transmission electron microscopic (TEM) analysis of the samples. Figure 1d shows the TEM images of PPy/Pt composite. The dispersion of the platinum particles in the PPy film can be observed from the TEM image. The platinum particles are seen as dark spots dispersed in the PPy matrix in the background. Moreover, in order to obtain the mean size of the platinum particles, the histogram of particle size distribution of platinum catalyst, was drawn (Fig. 1e). For the platinum catalyst, the mean particle size had a diameter of approximately 11 nm.

Figure 1f shows typical energy dispersive X-ray (EDX) analysis results for platinum nanoparticles dispersed into the PPy film. The Pt peak is clearly seen, which confirms that the platinum nanoparticles are synthesized in the PPy film.

Electrochemical Characterization of the GCE/PPy/Pt

To understand the electrochemical activity of the GCE/PPy/Pt, the cyclic voltammetric responses of the GCE/PPy/Pt and GCE/Pt were recorded at a scan rate

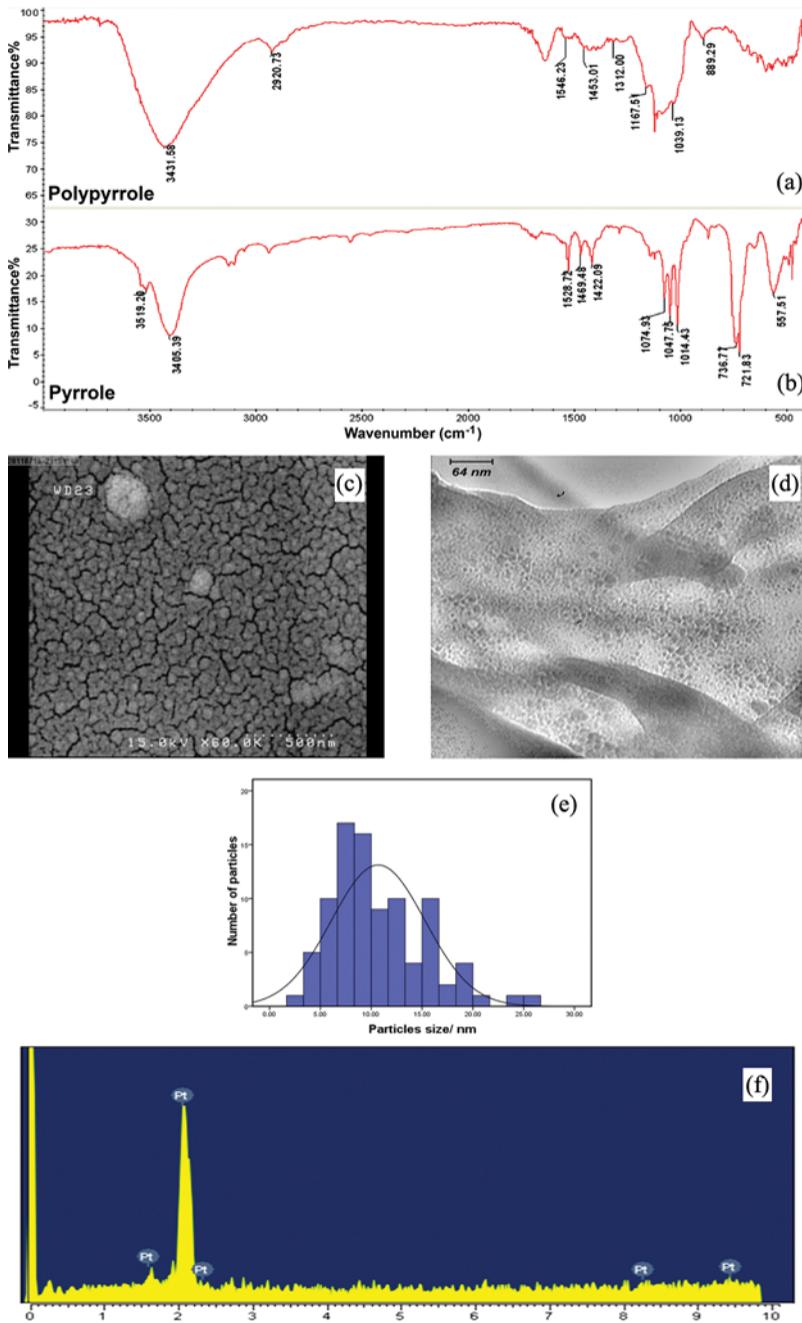


Figure 1. FTIR spectra of (a) pure polypyrrole, (b) pyrrole, (c) SEM image of GCE/PPy, (d) TEM image of GCE/PPy/Pt, (e) histogram of particle size distribution of platinum particles catalyst, and (f) EDX analysis results for platinum nanoparticles dispersed into PPy film. (Figure available in color online.)

of 50 mV s^{-1} . Figure 2a illustrates the cyclic voltammogram of the GCE/PPy/Pt in $0.3 \text{ mol L}^{-1} \text{ HClO}_4$. As depicted in Fig. 2a, three pairs of peaks (a/a', b/b', and c/c') are discernible. The oxidation and reduction peak couples (a/a' and b/b') correspond to desorption and adsorption of hydrogen atoms on the platinum surface, while the other pair (c/c') correspond to the formation of platinum oxide and its reduction, respectively. To the best of our knowledge, the electrocatalytic properties are expected to depend on the number of available surface sites, activities referred to real platinum surface area (A_r). Measurement of hydrogen adsorption is widely used in determining A_r (Trasatti and Petrii 1992; Croissant et al. 1998). The A_r of the deposited platinum was estimated from hydrogen adsorption on the voltammogram (Fig. 2a) according to the following equation:

$$A_r = Q_H/Q_0 \quad (3)$$

Q_0 has been commonly taken as $0.21 \text{ mC/real cm}^2$ (Brammer 1965). The Q_H is the charge consumed for hydrogen adsorption. Q_H can be obtained for GCE/PPy/Pt by integration of the current peak in a potential range -300 to 146 mV . The amounts of Q_H , A_r , and other physical characteristics of GCE/PPy/Pt and

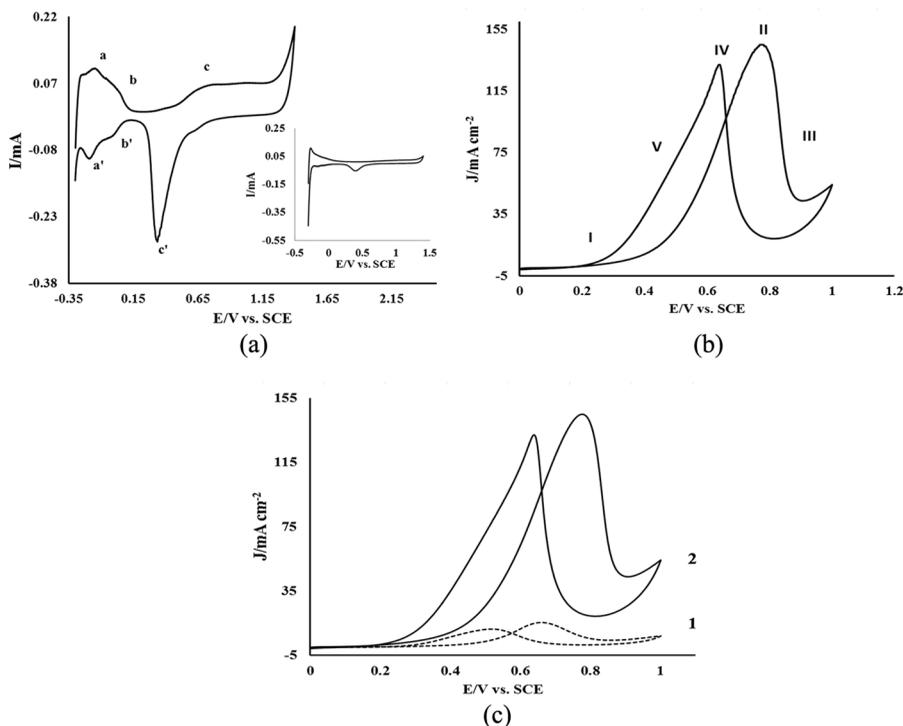


Figure 2. Cyclic voltammograms of (a) GCE/PPy/Pt (Inset shows the cyclic voltammogram of the GCE/Pt in the same conditions) in $0.3 \text{ mol L}^{-1} \text{ HClO}_4$, (b) GCE/PPy/Pt in 0.6 mol L^{-1} methanol, and (c) GCE/Pt (1) and GCE/PPy/Pt (2) in 0.6 mol L^{-1} methanol. The thickness of deposited polymer was $0.18 \mu\text{m}$ and amount of Pt: 0.6 mg cm^{-2} . Scan rate: 50 mV s^{-1} .

GCE/Pt are given in Table 1. The hydrogen adsorption charge values for GCE/PPy/Pt and GCE/Pt (inset in Fig. 2a) were calculated to be 0.47 and 0.05 mC, respectively. These results show that the actual active surface area of the GCE/PPy/Pt is about 10 times larger than that of the GCE/Pt. This observation suggests that when the Pt nanoparticles are incorporated into the PPy film, the catalytic reactivity of the electrode increases remarkably because of an increase in real surface area (A_r) of the electrode. Consequently, an estimation of A_r clearly reveals the effect of PPy film on the performance of the electrode reactivity toward the oxidation of methanol.

Table 1. Physical characteristics of GCE/PPy/Pt as determined from the charge corresponding to the hydrogen adsorption peaks in Fig. 2a

Electrode	GCE/PPy/Pt	GCE/Pt
Pt loading (mg cm^{-2})	0.6	0.6
Q_o (mC/real cm^2)	0.21	0.21
Q_H (mC)	0.47	0.05
A_g (cm^2)	0.0314	0.0314
A_r (real cm^2)	2.24	0.24
R_f ($\text{cm}^2/\text{real cm}^2$) ^a	71.34	7.64

^aRoughness factor [real surface area (A_r)/geometric surface area (A_g)].

Electrooxidation of Methanol

In order to evaluate the electrocatalytic performance of GCE/PPy/Pt for methanol oxidation, cyclic voltammetric measurements were carried out. Figure 2b shows the cyclic voltammogram for the GCE/PPy/Pt in $0.3 \text{ mol L}^{-1} \text{ HClO}_4$ containing 0.6 mol L^{-1} methanol. As is obvious from Fig. 2b, in the positive scan, the adsorption of methanol from the bulk of the solution on to the electrode surface and its successive dehydrogenation result in the formation of linearly bonded CO species at low overpotential (region I) (Ávila-García et al. 2010). By sweeping the potential to the more positive values, the anodic peak of methanol oxidation appears around +781 mV (region II), where the adsorbed OH species, from water decomposition may react with the adsorbed CO on the GCE/PPy/Pt and produce CO_2 , protons (H^+), electrons (e^-), a vacant site, and different species on the Pt surface such as HCHO and HCOOH (Krewer et al. 2006; Hamnett 1997; Antolini, Salgado, and Gonzalez 2006). At high potentials, the oxidation of Pt and formation of platinum oxides causes a decrease in the amount of active sites available on the electrode surface that subsequently results in a decrease of peak current density (region III). In the backward scan, the reduction of platinum oxides to platinum and production of active sites take place, so the re-oxidation of methanol and/or methanol residues occurs on clean platinum surface, and backward peak (region IV) appears (Li et al. 2002; Manoharan and Goodenough 1992). Finally, the current density decreases due to the surface blocking by linearly bonded CO (region V) (Gasteiger et al. 1993).

A cyclic voltammetric test was used to investigate the effect of the PPy film on the enhancement of platinum nanoparticles efficiency towards the catalytic oxidation

of methanol. Two typical cyclic voltammograms showing the electrooxidation of methanol at GCE/Pt and GCE/PPy/Pt are compared (Fig. 2c). Although the Pt loading for both electrodes are similar, it is clearly seen that the peak current for the oxidation of methanol increased from 15.25 mA cm^{-2} (for GCE/Pt) to 144.9 mA cm^{-2} (for GCE/PPy/Pt), confirming the crucial effect of the PPy film on the enhancement of platinum nanoparticles efficiency towards the catalytic oxidation of methanol. This effect is caused by high dispersion of platinum nanoparticles in polymer matrix and the synergistic effects of conducting polymer and metal particles (Leone, Marino, and Scharifker 1992; Zhong et al. 1996). Moreover, incorporation of platinum nanoparticles into this porous polymer causes a decrease in the poisoning effect of CO.

One more point which can be concluded from Fig. 2c is that the oxidation of methanol at GCE/Pt is delayed about 0.2 V with respect to GCE/PPy/Pt. This means that the polymer can improve to some extent the adsorption of methanol on the catalytic sites (Golabi and Nozad 2003).

Effect of Polymer Thickness

As cited by other workers (Pournaghi-Azar and Habibi 2007b; Pournaghi-Azar and Habibi-A 2005; Razmi and Habibi 2009), the electrocatalysis of methanol oxidation is sensitive to the thickness of the polymer film. One of the advantages of electrochemical polymerization is that the polymer film thickness can be easily calculated from the charge consumed (Q) during the electrodeposition of PPy film using Faraday's law. Figure 3a shows a plot of anodic peak current densities of GCE/PPy/Pt as a function of the thickness of the polymer. It can be seen that the anodic current densities rose progressively for a film thickness up to about $0.18 \mu\text{m}$, but by further increasing the film thickness from 0.18 to $0.45 \mu\text{m}$, the anodic current densities decreased and finally remained constant. The increase in the peak current density for the thickness of the polymer up to about $0.18 \mu\text{m}$ may be due to the occupation of platinum nanoparticles in the pores of polymer with the real sizes. The decrease in the anodic peak current densities for methanol oxidation beyond $0.18 \mu\text{m}$ may be due to the decrease in the film porosity, as a result of the formation of a compact layer of polymer film. This causes a decrease in the density of active sites available for methanol oxidation reaction. Furthermore, a thicker film leads to difficulties in electron transfer and diffusion of methanol through the film itself.

Effect of Platinum Loading

The effect of different platinum loadings ranging from 0.1 to 0.9 mg cm^{-2} at the PPy modified GCE surface on the oxidation of methanol was studied. Figure 3b illustrates the changes of the anodic peak current densities as a function of Pt loading. The anodic peak current densities increased with the amount of Pt from 0.1 to 0.6 mg cm^{-2} and reached a nearly constant value at higher amounts of Pt. At the lower platinum depositions, platinum nanoparticles are almost uniformly deposited on the surface of the PPy modified GCE and the real area of platinum particles increased that caused an enhancement in the electrocatalytic activity of the modified electrode. But any extra platinum deposition did not increase the

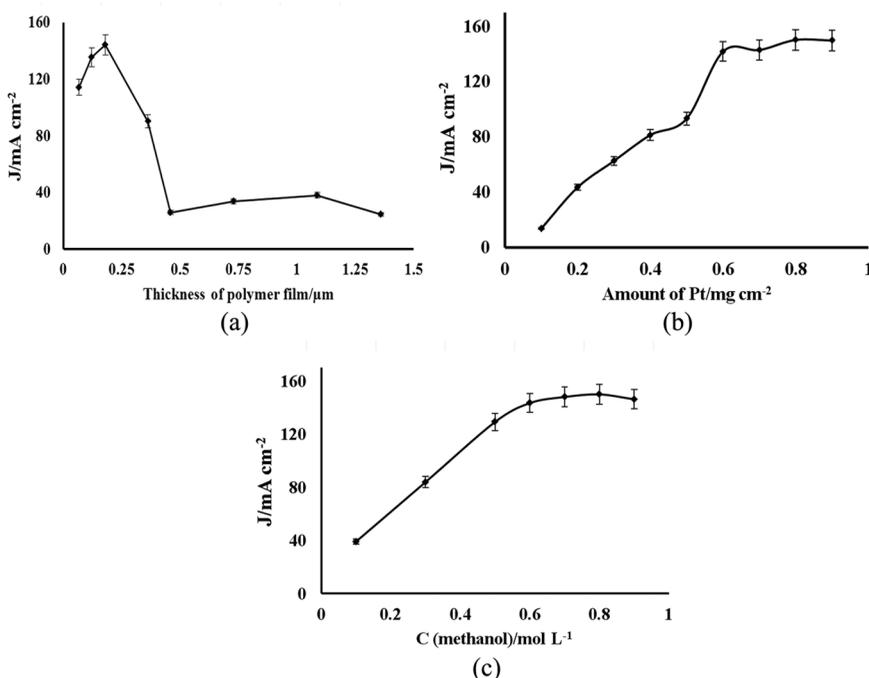


Figure 3. Plot of anodic peak current densities of (a) GCE/PPy/Pt containing 0.6 mol L^{-1} methanol as a function of the thickness of polymer, (b) GCE/PPy/Pt containing 0.6 mol L^{-1} methanol as a function of platinum loading, and (c) methanol oxidation as a function of methanol concentration. The thickness of deposited polymer was $0.18 \mu\text{m}$ and amount of Pt: 0.6 mg cm^{-2} . In $0.3 \text{ mol L}^{-1} \text{ HClO}_4$. Scan rate: 50 mV s^{-1} .

catalytic activity of the electrodes, probably because of a constant active surface area. Accordingly, because the anodic peak current densities did not increase significantly after 0.6 mg cm^{-2} , this amount of Pt nanoparticles was considered as an optimum value and was chosen for Pt deposition in all experiments.

Effect of Methanol Concentration

The effect of methanol concentration on the anodic peak current densities of methanol oxidation was examined. Figure 3c illustrates a plot of anodic peak current densities of GCE/PPy/Pt as a function of methanol concentration. According to the experimental data, the anodic peak current densities increased with methanol concentration, and leveled off at concentrations higher than 0.6 mol L^{-1} . This effect may be due to saturation of active sites at the surface of electrode.

Effect of Scan Rate

The influence of the scan rate (ν) on the electrooxidation of methanol at the GCE/PPy/Pt was investigated and the results are graphically shown in Fig. 4a. In principle, the peak currents are proportional to the ν for an adsorption process

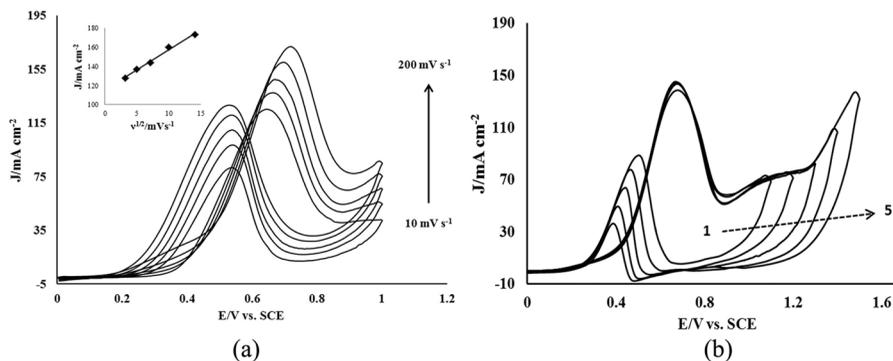


Figure 4. Cyclic voltammograms of GCE/PPy/Pt in $0.3 \text{ mol L}^{-1} \text{ HClO}_4$ containing 0.6 mol L^{-1} methanol (a) at different scan rates: (from inner to outer) $10, 25, 50, 100,$ and 200 mV s^{-1} (Inset: variations of anodic peak current densities with $\nu^{1/2}$); and (b) at different forward potential scan limits: (1) $0.0\text{--}1.1 \text{ V}$, (2) $0.0\text{--}1.2 \text{ V}$, (3) $0.0\text{--}1.3 \text{ V}$, (4) $0.0\text{--}1.4 \text{ V}$, and (5) $0.0\text{--}1.5 \text{ V}$. The thickness of deposited polymer was $0.18 \mu\text{m}$ and amount of Pt: 0.6 mg cm^{-2} .

and $\nu^{1/2}$ for a diffusion process (Bard and Faulkner 2001). As is obvious from Fig. 4a, there is a relationship between the anodic peak current densities and scan rates. In order to emphasize the relationship, a plot of anodic peak current densities vs. $\nu^{1/2}$ was drawn (inset in Fig. 4a). The results imply that the anodic peak current densities are linearly proportional to $\nu^{1/2}$. This finding reveals that the electrocatalytic oxidation of methanol at the GCE/PPy/Pt is a diffusion-controlled process.

Effect of Forward Potential Scan Limit

Figure 4b shows cyclic voltammograms of methanol oxidation on GCE/PPy/Pt for different final potential scan limits. By increasing the final positive potential limit, the anodic peak current densities of methanol oxidation remain unchanged, but the reoxidation peak current densities are decreased. Indeed by increasing the final positive potentials, the conversion of platinum to platinum oxide was accelerated and caused a decrease in reoxidation peak current densities, because the methanol molecules were only oxidized on a fresh metallic platinum surface (Parsons and Van der Noot 1988). In addition to this, inspection of Fig. 4b reveals that the potential of methanol oxidation peak remains invariable, while the reoxidation peak potential shifts to the negative values, because of stabilization of oxidative platinum surfaces in high potentials; hence it needs more negative potentials to reduce platinum oxide in the backward scan.

Chronoamperometric Studies

Figure 5a illustrates the chronoamperograms (current-time transients) which are recorded for the oxidation of methanol on GCE/PPy/Pt at different potential steps (0.4 and 0.6 V vs. SCE) for 2000 s . It is seen that the current degraded rapidly for 500 s , which could be due to the formation of intermediate species during methanol oxidation reaction (Kabbabi et al. 1998). The signal then became relatively stable. The initial high current corresponded mainly to double layer charging. As

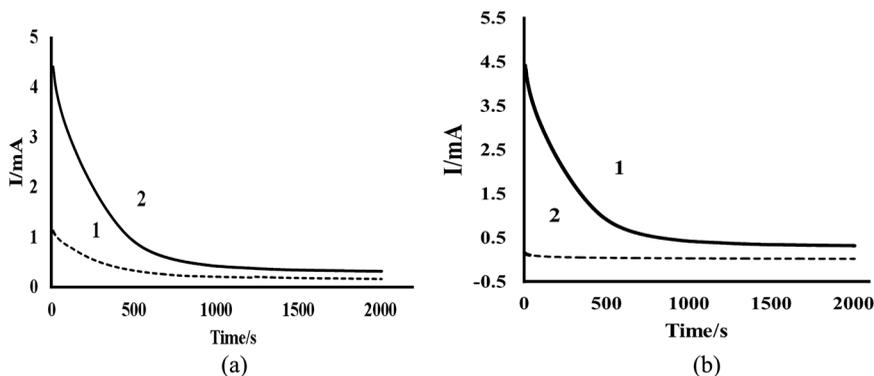


Figure 5. (a) Long-time amperometric response of GCE/PPy/Pt, at different potentials: (1) 0.4, (2) 0.6; and (b) chronoamperometric curves of (1) GCE/PPy/Pt and (2) GCE/Pt at 0.6 V, in 0.3 mol L^{-1} HClO_4 containing 0.6 mol L^{-1} methanol. The thickness of deposited polymer was $0.18 \mu\text{m}$ and amount of Pt: 0.6 mg cm^{-2} .

shown in Fig. 5a, the current of plateau at potential of 0.6 V was higher than 0.4 V, because this potential is close to the potential of anodic peak in the cyclic voltammogram (see Fig. 2b). In addition, the chronoamperometric measurements of methanol electrooxidation at the GCE/PPy/Pt and GCE/Pt were investigated. Figure 5b shows the chronoamperograms of these electrodes when the potential was fixed at 0.6 V. As is depicted in Fig. 5b, the GCE/PPy/Pt displayed much higher current than that of the GCE/Pt after 2000 s. These results confirm that the electrocatalytic activity of the GCE/PPy/Pt was higher than that of the GCE/Pt due to the presence of PPy matrix.

Kinetic Analysis of Methanol Oxidation

Tafel plots. Figure 6a shows Tafel plots for methanol oxidation at GCE/PPy/Pt prepared with different amounts of Pt nanoparticles. The data in Fig. 6a may be considered more quantitatively by examining several kinetic parameters. Table 2 summarizes the kinetic data for methanol oxidation at the GCE/PPy/Pt prepared with different amount of Pt nanoparticles. The Tafel slopes refer to plots of $\log J$ vs. potential for methanol oxidation in 0.3 mol L^{-1} HClO_4 , and the exchange current density (J_0) was determined by extrapolating to zero overpotential. From Fig. 6a and Table 2, we can distinguish that the methanol oxidation at the GCE/PPy/Pt was affected by the amount of the platinum nanoparticles on the GCE/PPy. In Fig. 6b, values of $\log J_0$ were plotted as a function of the amount of Pt. It is clearly seen that the exchange current densities of the prepared electrodes increased as the amount of Pt increases from 0.2 to 0.6 mg cm^{-2} and then diminished.

We also used Tafel studies to elucidate the effect of the PPy film on the electrocatalytic activity of Pt nanoparticles. For this reason, the exchange current density (J_0) of methanol oxidation at different electrodes was investigated. The polarization studies on GCE/PPy/Pt and GCE/Pt were carried out and typical Tafel curves are shown in Fig. 6c. According to the Tafel equation (Wang 2000), the values of J_0 at

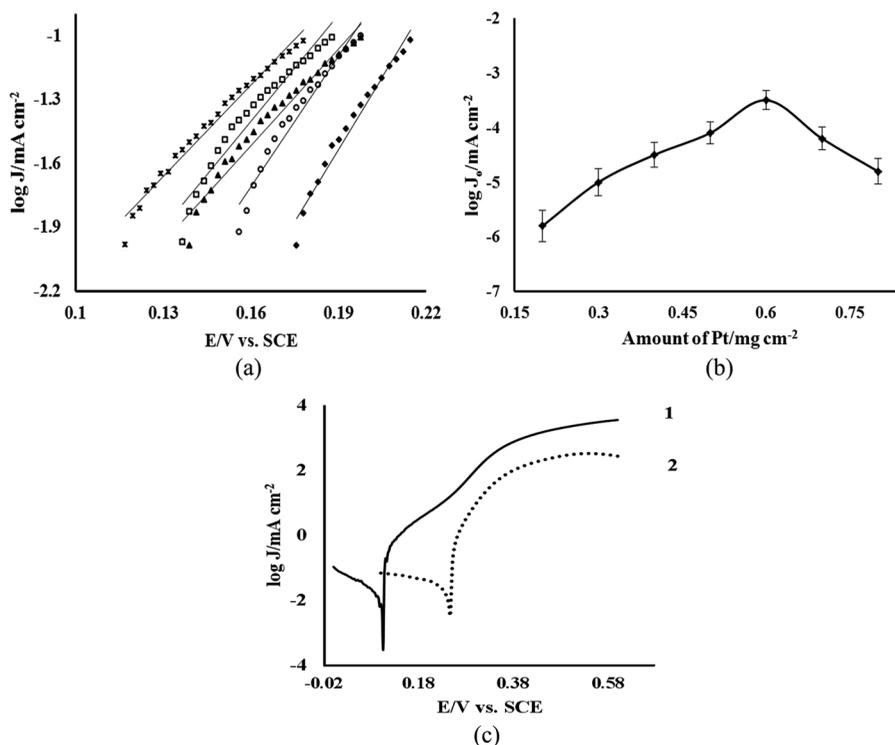


Figure 6. (a) Tafel plots for methanol oxidation at the GCE/PPy/Pt for different Pt depositions: 0.2 (◆), 0.3 (○), 0.4 (▲), 0.5 (□) and 0.6 mg cm^{-2} (*) at a scan rate of 2 mV s^{-1} ; (b) plot of exchange current density (J_o) for methanol oxidation at the GCE/PPy/Pt as a function of amount of Pt; and (c) Tafel plots of (1) GCE/PPy/Pt and (2) GCE/Pt at a scan rate of 2 mV s^{-1} .

GCE/PPy/Pt and GCE/Pt were calculated to be equal to $0.3 \mu\text{A cm}^{-2}$ and $0.23 \times 10^{-7} \mu\text{A cm}^{-2}$, respectively. Comparison of the exchange current densities shows that the J_o value of the GCE/PPy/Pt is approximately 1.3×10^7 times higher than that of the GCE/Pt. The obtained results indicate that the existence of PPy film significantly accelerated the process of methanol electrooxidation.

Table 2. Tafel parameters for methanol oxidation at the GCE/PPy/Pt

Amount of Pt (mg cm^{-2})	$-\log J_o$ (mA cm^{-2})	Slope (V^{-1})	Transfer coefficient α
0.7	4.2	17.66	0.48
0.6	3.5	14.35	0.57
0.5	4.1	16.65	0.51
0.4	4.5	15.13	0.55
0.3	5.0	20.60	0.39
0.2	5.8	22.59	0.33

Catalytic efficiency. In order to compare the catalytic efficiency of different electrodes, we investigated anodic peak current densities of different electrodes.

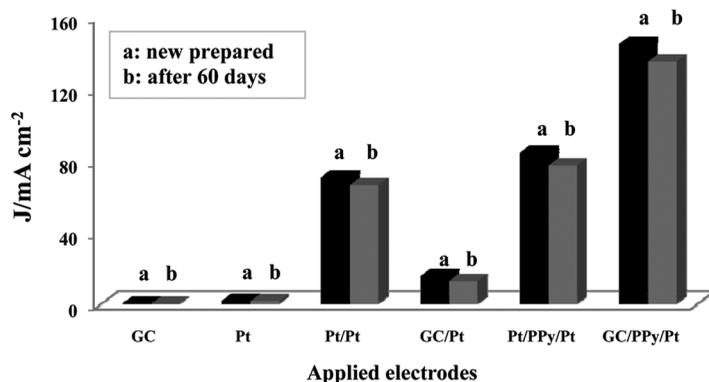


Figure 7. Histograms of anodic peak current densities of methanol oxidation appeared at different electrodes in $0.3 \text{ mol L}^{-1} \text{ HClO}_4$ containing 0.6 mol L^{-1} methanol. The thickness of deposited polymer was $0.18 \mu\text{m}$ and amount of Pt: 0.6 mg cm^{-2} . Scan rate, 50 mV s^{-1} .

Figure 7 depicts the anodic current densities of methanol electrooxidation at the surface of these electrodes (a) immediately after preparation of electrodes and (b) after storing of them for 60 days in the laboratory atmosphere. GCE/PPy/Pt and Pt/PPy/Pt were catalytically more active than the other electrodes and they had relatively high stability when stored in ambient conditions. The higher catalytic efficiency of these two electrodes may be attributed to the high dispersion of the platinum nanoparticles in the polymer matrix which provides electrodes with higher surface areas and, hence, enhanced the electrocatalytic activities of these two electrodes toward the oxidation of methanol molecules.

CONCLUSIONS

A nanocomposite film of PPy/Pt was synthesized electrochemically at the surface of GCE. Characterization of this electrode by different techniques (i.e., IR, SEM, TEM, and EDX) confirmed the synthesis of PPy film and the existence of platinum nanoparticles in the PPy film at the surface of the electrode. We have demonstrated by means of different electrochemical studies that GCE/PPy/Pt had much higher electrochemical activity toward the oxidation of methanol compared to smooth platinum and platinum nanoparticles modified electrodes. The observed improvement is attributed to the high dispersion of platinum nanoparticles in the PPy film and the synergistic effects of conducting polypyrrole and platinum nanoparticles. The prepared electrodes exhibited satisfactory stability and reproducibility when stored in ambient conditions. Factors such as the thickness of PPy film, amount of platinum, and methanol concentration all significantly influenced the anodic current densities of electrooxidation of methanol at the GCE/PPy/Pt.

REFERENCES

- Antolini, E., J. R. C. Salgado, and E. R. Gonzalez. 2006. The methanol oxidation reaction on platinum alloys with the first row transition metals: The case of Pt–Co and –Ni alloy electrocatalysts for DMFCs: A short review. *Appl. Catal. B* 63: 137–149.

- Ávila-García, I., C. Ramírez, J. M. Hallen López, and E. M. Arce Estrada. 2010. Electrocatalytic activity of nanosized Pt alloys in the methanol oxidation reaction. *J. Alloy Compd.* 495: 462–465.
- Bard, A. J., and L. R. Faulkner. 2001. *Electrochemical methods*. New York, NY: J. Wiley and Sons.
- Beck, F., R. Michaelis, F. Schloten, and B. Zinger. 1994. Film forming electropolymerization of pyrrole on iron in aqueous oxalic acid. *Electrochim. Acta* 39: 229–234.
- Beden, B., F. Hahn, S. Juanto, C. Lamy, and J. M. Leger. 1987. Infrared spectroscopic study of the methanol adsorbates at a platinum electrode: Part I. Influence of the bulk concentration of methanol upon the nature of the adsorbates. *J. Electroanal. Chem.* 225: 215–225.
- Biallozor, S., A. Kupniewska, and V. Jasulaitene. 2003. Electro-oxidation of methanol and ethanol on poly (3,4-Ethylenedioxythiophene) with dispersed Pt, Pt + Sn, and Pt + Pb particles. *Fuel Cells* 3: 8–14.
- Bouzek, K., K. M. Mangold, and K. Jüttner. 2001. Electrocatalytic activity of platinum modified polypyrrole films for the methanol oxidation reaction. *J. Appl. Electrochem.* 31: 501–507.
- Brammer, S. B. 1965. The use of large anodic galvanostatic transients to evaluate the maximum adsorption on platinum from formic acid solutions. *J. Phys. Chem.* 69: 562–571.
- Cai, L. T., and H. Y. Chen. 1998. Preparation and electroactivity of polyaniline/poly (acrylic acid) film electrodes modified by platinum microparticles. *J. Appl. Electrochem.* 28: 161–166.
- Castro Luna, A. M. 2000. A novel electrocatalytic polyaniline electrode for methanol oxidation. *J. Appl. Electrochem.* 30: 1137–1142.
- Chen, C. C., C. S. C. Bose, and K. Rajeshwar. 1993. The reduction of dioxygen and the oxidation of hydrogen at polypyrrole film electrodes containing nano dispersed platinum particles. *J. Electroanal. Chem.* 350: 161–176.
- Chen, W., X. Li, G. Xue, Z. Wang, and W. Zou. 2003. Magnetic and conducting particles: Preparation of polypyrrole layer on Fe₃O₄ nanospheres. *Appl. Surf. Sci.* 218: 216–222.
- Croissant, M. J., T. Napporn, J. M. Lećger, and C. Lamy. 1998. Electrocatalytic oxidation of hydrogen at platinum–modified polyaniline electrodes. *Electrochim. Acta* 43: 2447–2457.
- Del Valle, M. A., F. R. Díaz, M. E. Bodini, T. Pizarro, R. Córdoba, H. Gómez, and R. Schrebler. 1998. Polythiophene, polyaniline and polypyrrole electrodes modified by electro-deposition of Pt and Pt/Pb for formic acid electrooxidation. *J. Appl. Electrochem.* 28: 943–946.
- Gasteiger, H. A., N. Markovic, P. N. Ross, and E. J. Cairns. 1993. Methanol electrooxidation on well characterized platinum ruthenium bulk alloys. *J. Phys. Chem.* 97: 12020–12029.
- Golabi, S. M., and A. Nozad. 2003. Electrocatalytic oxidation of methanol at lower potentials on glassy carbon electrode modified by platinum and platinum alloys incorporated in poly (*o*-Aminophenol) film. *Electroanalysis* 15: 278–286.
- Habibi, B., M. H. Pournaghi-Azar, H. Abdolmohammad-Zadeh, and H. Razmi. 2008. Electrochemical preparation of a novel, effective and low cost catalytic surface for hydrogen evolution reaction. *Int. J. Hydrogen Energ.* 34: 2668–2678.
- Habibi, B., M. H. Pournaghi-Azar, H. Abdolmohammad-Zadeh, and H. Razmi. 2009. Electrocatalytic oxidation of methanol on mono and bimetallic composite films: Pt and Pt–M (M = Ru, Ir and Sn) nano-particles in poly (*o*-aminophenol). *Int. J. Hydrogen Energ.* 34: 2880–2892.
- Hable, C. T., and M. S. Wrighton. 1993. Electrocatalytic oxidation of methanol and ethanol: A comparison of platinum–tin and platinum–ruthenium catalyst particles in a conducting polyaniline matrix. *Langmuir* 9: 3284–3290.
- Hammache, H., L. Makhouloufi, and B. Saidani. 2001. Electrocatalytic oxidation of methanol on PPy electrode modified by gold using the cementation process. *Synth. Met.* 123: 515–522.

- Hamnett, A. 1997. Mechanism and electrocatalysis in the direct methanol fuel cell. *Catal. Today* 38: 445–457.
- He, C., H. R. Kunz, and J. M. Fenton. 1997. Evaluation of platinum-based catalysts for methanol electro-oxidation in phosphoric acid electrolyte. *J. Electrochem. Soc.* 144: 970–979.
- Kabbabi, A., R. Faure, R. Durand, B. Beden, F. Hahn, J. M. Léger, and C. Lamy. 1998. In situ FTIRS study of the electrocatalytic oxidation of carbon monoxide and methanol at platinum–ruthenium bulk alloy electrodes. *J. Electroanal. Chem.* 444: 41–53.
- Kanazawa, K. K., A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, G. P. Gardini, and J. F. Kwak. 1979. Polypyrrole: An electrochemically synthesized conducting organic polymer. *Synth. Met.* 1: 329–336.
- Kelaidopoulou, A., E. Abelidou, A. Papoutsis, E. K. Polychroniadis, and G. Kokkinidis. 1998. Electrooxidation of ethylene glycol on Pt-based catalysts dispersed in polyaniline. *J. Appl. Electrochem.* 28: 1101–1106.
- Kessler, T., and A. M. Castro Luna. 2002. A catalytic platinum–ruthenium–polyaniline electrode for methanol oxidation. *J. Appl. Electrochem.* 32: 825–830.
- Krewer, U., M. Christov, T. Vidakovic, and K. Sundmacher. 2006. Impedance spectroscopic analysis of the electrochemical methanol oxidation kinetics. *J. Electroanal. Chem.* 589: 148–159.
- Kulesza, P. J., M. Matczak, A. Wolkiewicz, B. Grzybowska, M. Galkowski, M. A. Malik, and A. Wieckowski. 1999. Electrocatalytic properties of conducting polymer based composite film containing dispersed platinum microparticles towards oxidation of methanol. *Electrochim. Acta* 44: 2131–2137.
- Leone, A., W. Marino, and B. R. Scharifker. 1992. Electrodeposition and electrochemical behavior of palladium particles at polyaniline and polypyrrole films. *J. Electrochem. Soc.* 139: 438–443.
- Li, W. S., L. P. Tian, Q. M. Huang, H. Li, H. Y. Chen, and X. P. Lian. 2002. Catalytic oxidation of methanol on molybdate-modified platinum electrode in sulfuric acid solution. *J. Power Sources* 104: 281–288.
- Liu, H., C. Song, L. Zhang, J. Zhang, H. Wang, and D. P. Wilkinson. 2006. A review of anode catalysis in the direct methanol fuel cell. *J. Power Sources* 155: 95–110.
- Liu, L., C. Pu, R. Viswanathan, Q. Fan, R. Liu, and E. S. Smotkin. 1998. Carbon supported and unsupported Pt–Ru anodes for liquid feed direct methanol fuel cells. *Electrochim. Acta* 43: 3657–3663.
- Manoharan, R., and J. B. Goodenough. 1992. Methanol oxidation in acid on NiTi. *J. Mater. Chem.* 2: 875–887.
- Mikhaylova, A. A., E. B. Molodkina, O. A. Khazova, and V. S. Bagotzky. 2001. Electrocatalytic and adsorption properties of platinum microparticles electrodeposited into polyaniline films. *J. Electroanal. Chem.* 509: 119–127.
- Mulligan, R. F., A. A. Iliadias, U. Lee, and P. Kofinas. 2001. Synthesis of self-assembled metal-oxide nanostructures in a diblock copolymer matrix and intergration onto semiconductor surfaces. *Mater. Res. Soc. Symp. Proc.* 642: J2.11.1–J2.11.5.
- Niu, L., Q. Li, F. Wei, X. Chen, and H. Wang. 2003a. Electrochemical impedance and morphological characterization of platinum-modified polyaniline film electrodes and their electrocatalytic activity for methanol oxidation. *J. Electroanal. Chem.* 544: 121–128.
- Niu, L., Q. Li, F. Wei, X. Chen, and H. Wang. 2003b. Formation optimization of platinum-modified polyaniline films for the electrocatalytic oxidation of methanol. *Synth. Met.* 139: 271–276.
- Niu, L., Q. Li, F. Wei, S. Wu, P. Liu, and X. Cao. 2005. Electrocatalytic behavior of Pt-modified polyaniline electrode for methanol oxidation: Effect of Pt deposition modes. *J. Electroanal. Chem.* 578: 331–337.

- Parsons, R., and T. Van der Noot. 1988. The oxidation of small organic molecules: A survey of recent fuel cell related research. *J. Electroanal. Chem.* 257: 9–45.
- Pournaghi-Azar, M. H., and B. Habibi-A. 2005. 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: 23–34.
- Pournaghi-Azar, M. H., and B. Habibi. 2007a. Electrocatalytic oxidation of methanol on poly (phenylenediamines) film palladized aluminum electrodes, modified by Pt micro-particles: Comparison of permselectivity of the films for methanol. *J. Electroanal. Chem.* 601: 53–62.
- Pournaghi-Azar, M. H., and B. Habibi. 2007b. Nickel hexacyanoferrate film immobilized on the aluminum electrode as an inorganic matrix for dispersion of platinum and some platinum alloys particles for electrocatalytic oxidation of methanol. *J. Electroanal. Chem.* 605: 136–144.
- Rajendra Prasad, K., and N. Munichandraiah. 2002. Electrooxidation of methanol on polyaniline without dispersed catalyst particles. *J. Power Sources* 103: 300–304.
- Razmi, H., and E. Habibi. 2009. Electrocatalytic oxidation of methanol on carbon ceramic electrode modified by platinum nanoparticles incorporated in poly (*o*-phenylenediamine) film. *J. Solid State Electrochem.* 13: 1897–1904.
- Saffarian, H. M., R. Srinivasan, D. Chu, and S. Gilman. 1998. Area determination in fractal surfaces of Pt and Pt–Ru catalysts for methanol oxidation. *Electrochim. Acta* 44: 1447–1454.
- Selvaraj, V., M. Alagar, and I. Hamerton. 2006. Electrocatalytic properties of monometallic and bimetallic nanoparticles-incorporated polypyrrole films for electro-oxidation of methanol. *J. Power Sources* 160: 940–948.
- Shen, P. K., and A. C. C. Tseung. 1994. Anodic oxidation of methanol on Pt/WO₃ in acidic media. *J. Electrochem. Soc.* 141: 3082–3090.
- Shimazu, K., D. Weisshaar, and T. Kuwana. 1987. Electrochemical dispersion of Pt micro-particles on glassy carbon electrodes. *J. Electroanal. Chem.* 223: 223–234.
- Swathirajan, S., and Y. M. Mikhail. 1992. Methanol oxidation on platinum–tin catalysts dispersed on poly (3–methyl) thiophene conducting polymer. *J. Electrochem. Soc.* 139: 2105–2110.
- Trasatti, S., and O. A. Petrii. 1992. Real surface area measurements in electrochemistry. *J. Electroanal. Chem.* 327: 353–376.
- Vishnuvardhan, T. K., V. R. Kulkarni, C. Basavaraja, and S. C. Raghavendra. 2006. Synthesis, characterization and a.c. conductivity of polypyrrole/Y₂O₃ composites. *Bull. Mater. Sci.* 29: 77–83.
- Wang, J. 2000. *Analytical electrochemistry*, 2nd edition. New York, NY: Wiley-VCH.
- Wasmus, S., and A. Kuver. 1999. Methanol oxidation and direct methanol fuel cells: A selective review. *J. Electroanal. Chem.* 461: 14–31.
- Yano, J., T. Shiraga, and A. Kitani. 2008. Dispersed platinum and tin polyaniline film electrodes for the anodes of the direct methanol fuel cell. *J. Solid State Electrochem.* 12: 1179–1182.
- Yassar, A., J. Roncali, and F. Garnier. 1988. Preparation and electroactivity of poly (thiophene) electrodes modified by electrodeposition of palladium particles. *J. Electroanal. Chem.* 255: 53–69.
- Zhao, Y., X. Yang, J. Tian, F. Wang, and L. Zhan. 2010. A facile and novel approach toward synthetic polypyrrole oligomers functionalization of multi walled carbon nanotubes as PtRu catalyst support for methanol electro-oxidation. *J. Power Sources* 195: 4634–4640.
- Zhong, Q., L. Xiong, Z. Zhong, and W. Li. 1996. Synergistic effect of the oxidation of formic acid at polyaniline electrodes modified by palladium microparticles. *Acta Phys. Chim. Sin.* 12: 346–352.