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Electrocatalytic Oxidation of Methanol using Fluorine-Tin Oxide Electrode Modified with Platinum and Osmium Nanoparticles Dispersed into Montmorillonite Clay Film

Ibtihal Hashim Azeez Al-Omairi, Behjat Deiminiat, Gholam Hossein Rounaghi,* and Simin Kolahi-Ahari

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

*Corresponding Author, Tel.: +98-5137626388

E-Mails: ghrounaghi@yahoo.com; ronaghi@um.ac.ir

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Abstract- A new nanocatalyst was prepared using montmorillonite (MMT) clay mineral as a low-cost substrate incorporation with platinum and osmium nanoparticles for electrocatalytic oxidation of methanol molecules. The morphology and microscopic structure of the nanocomposite film formed at the surface of the fluorine tin oxide (FTO) electrode, were characterized by scanning electron microscopy and energy dispersive X-ray analysis. The electrocatalytic activity of the Pt-Os/Clay/FTO modified electrode was compared with Pt/FTO and Pt/Clay/FTO electrodes using cyclic voltammetry and chronoamperometry techniques and it was found that the Pt-Os/Clay/FTO electrode has a better performance for oxidation of methanol molecules. The exchange current density (J_0) values for Pt/FTO, Pt/Clay/FTO and Pt-Os/Clay/FTO were calculated using the Tafel equation and they were found to be: 2.48×10^{-6}, 4.01×10^{-6} and 8.45×10^{-6} mA cm^{-2}, respectively. The results indicate that the purposed electrode accelerates significantly the process of methanol electrooxidation. The effects of various parameters on the electro-oxidation of methanol molecules were investigated and the obtained experimental results were discussed. The new modified electrode, showed a significant electrocatalytic activity for methanol electrooxidation over the other Pt-modified electrodes.

Keywords- Fluorine tin oxide; Montmorillonite; Clay; Platinum-osmium nanoparticles; Electrooxidation of methanol

1. INTRODUCTION

In recent years, the increasing energy consumption, the limited fossil fuel resources, and the environmental pollution throughout the world have endangered the future of human life. Therefore, it is urgent to find noble energy sources and use the methods to improve energy efficiency [1,2]. Today, there is a growing interest in the development of fuel cells, because they are clean energy conversion devices that can directly convert chemical energy to electrical energy with higher efficiency [3-5].

Low-molecular-weight alcohols are suitable and alternative materials in fuel cells. Direct alcohol fuel cells (DAFCs) are one of the most promising fuels due to the relatively simple transportation of fuel and portable electronic sources [6-8].

Direct methanol fuel cell is a kind of direct alcohol fuel cell and it is an emerging technology that has attracted much attention [9]. Liquid methanol is fed directly to the anode without any modification [10-12]. The methanol molecules which have a good electrochemical activity are continuously available, biodegradable, and relatively inexpensive. Methanol is easily transported and stored which makes it good fuel for fuel cells [13,14].

Recently, there has been a growing interest in nanocatalysts, especially platinum nanoparticles, for the electrooxidation of methanol molecules in fuel cells. But, Pt is very expensive and also it can be rapidly poisoned by the CO intermediate which is produced during the methanol electrooxidation [15-17]. To promote the electrooxidation process of methanol molecules and for decreasing the poisoning phenomena, several types of research have been proposed. These include alloying the Pt with metals such as Sn, Os, Al, Cr, Pd, Ru, Rh, and Cu to enhance the oxygen reduction reaction. Besides, the presence of a second metal on the nanoparticle surface, can improve the electrocatalytic properties of the electrodes and also increasing the tolerance to CO molecules.

Inorganic materials offer great advantages because of their chemical and mechanical properties and more stability [18,19]. Montmorillonite and the related clays, are known to be efficient and some previous studies already exist concerning this clay's role in coating to modify the electrochemical properties of the electrode surfaces. Montmorillonite is regarded as the most familiar and attractive member of the inorganic materials for methanol electrooxidation due to its chemical stability, ion exchange, abundance, easy access, cheapness, and cost-effectiveness in the use of clay in the construction of the modified electrodes [20]. Moreover, the pore-like structure of MMT can remarkably enhance the efficiency of the proposed electrode [21, 22]. The incorporation of MMT as catalyst support with the Pt particles can reduce the cost of the production of catalysts. Both of them can interact with each other and then function through a synergistic effect.

In the need of developing electrocatalysts to enhance the methanol electrooxidation efficiency, the present work is focused on platinum and osmium alloy nanoparticles to modify the FTO electrode.

The goal of the present work is to develop a novel, simple, low cost and easy preparation modified electrode for enhancing the electro-oxidation of methanol molecules. Silicate is an environmentally friendly and available material with a porous structure which makes it ideal support for fuel cells. The nature of the secondary metal, as well as the silicate layers of montmorillonite clay, has a large effect on the performance of the modified electrode. By using montmorillonite clay and a two-component catalyst (Pt–Os), the electrocatalytic efficiency for methanol oxidation increases. In addition, the modified Pt-Os/Clay/FTO electrode is disposable without any memory effect compared to the commercial electrodes which improves the electooxidation process of methanol molecules at the electrode surface. More discussion and the results which are obtained in this research work can be found in the next section.

2. EXPERIMENTAL

2.1. Chemicals

Montmorillonite was obtained from Sigma-Aldrich (USA). Methanol, perchloric acid, hexachloroplatinic (IV) acid hexahydrate, and sulfuric acid were purchased from Merck chemical company. All the other chemicals and reagents used in this work were of analytical grade and used without further purification. All solutions were prepared in deionized distilled water.

2.2. Instrumentation

All electrochemical measurements were performed using a μ-Autolab III (Eco Chemie, The Netherlands) potentiostat/galvanostat equipped with NOVA software at room temperature. A conventional three-electrode system was used with a FTO electrode, an Ag/AgCl (Azar Electrode Co., Urmia, Iran), and a platinum wire electrode (Metrohm) as the working, reference, and counter electrodes, respectively. The fluorine-doped tin oxide (8Ω, 5×5 cm) was purchased from Solaronix (Switzerland).

The morphology of the fabricated electrodes was characterized by using a LEO 1450VP SEM (Germany). Surface elemental analysis of the electrode was performed by the energy-dispersive X-ray (EDX) technique using Oxford-7353 EDX microanalyzer. Electrochemical impedance spectroscopy studies were carried out using Gill AC potentiostat.

2.3. Preparation of the modified electrode

A glass plate with FTO nanostructure on its surface, was selected with dimensions of 5 by 20 mm. As the first cleaning process, the FTO plate was rinsed for 10 min in a solution containing double distilled water and soap. In the next step, it was sonicated sequentially for 5 min in isopropanol, 5 min in ethanol, and 2 min in acetone. After drying the plats at room temperature, 20 mL of a homogeneous ink solution containing 10.0 mg of MMT in 10 mL of

double distilled water was dropped onto the surface of a FTO electrode, and then dried with an IR lamp. For electrochemical deposition of platinum and osmium nanoparticles on Clay/FTO electrode, an aqueous solution containing 2 mmol L^{-1} $H_2PtCl_6.6H_2O$, 0.4 mmol L-1 $OsCl_3$, and 0.2 mol L^{-1} $HClO_4$ was used. The electrochemical deposition of platinum nanoparticles was performed by using a potentiostatic technique at a constant potential of -0.2 V.

3. RESULTS AND DISCUSSION

3.1. Structural characterization

The surface morphology of the bare FTO, Clay/FTO and Pt-Os/Clay/FTO electrodes was investigated by SEM. As is evident in Fig. 1A, the surface of the FTO electrode has a uniform coverage with high porosity which increases the surface area of the electrode. The EDX spectrum (Fig. 1B) indicates the presence of the Sn elements. Figure 1C, exhibits the SEM image of the MMT clay on the FTO surface.

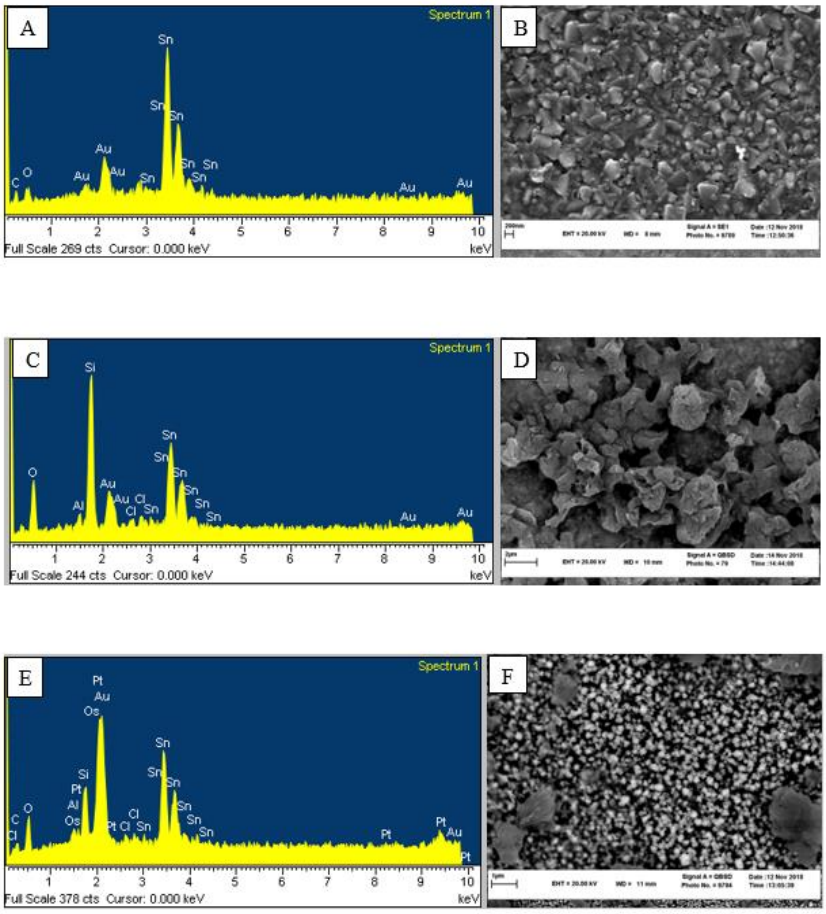

Figure 1. The SEM image (A) and EDX spectrum (B) of the bare FTO, the SEM image (C) and EDX spectrum (D) of Clay/FTO and the SEM image (E) and EDX spectrum (F) of Pt-Os/Clay/FTO.

In this Figure, a rough surface with an irregular structure is observed and the Si and Al peaks clearly (Fig. 1D) show the successful dispersion of the MMT clay at the surface of the FTO electrode. After deposition of Pt and Os on Clay/FTO electrode (Fig. 1E), Pt and Os nanoparticles are formed as a homogeneous shape and it seems that the MMT clay acts as good support. The EDX results in Fig. 1F, confirm that the distributions of Pt and Os nanoparticles are achieved predominantly on the surface of MMT clay.

3.2. Methanol electrooxidation

Fig. 2, illustrates the CV of the methanol molecules electrooxidation on Pt-Os /Clay/FTO electrode in 0.3 M $HClO_4$ and 0.6 M methanol solution. As depicted in Fig. 2, in the anodic going potential sweep, the methanol molecules are adsorbed from the bulk of the solution onto the electrode surface which results in the formation of linearly bonded CO species at low overpotential (region I) [23]. By sweeping potential to the more positive values, the oxidation peak of methanol molecules appears around 0.76 V (region II), and the adsorbed water molecules react with the CO intermediate at the surface of the modified electrode [13]. So, according to the following reactions, CO_2, H^+ and e^- or different species such as HCHO and HCOOH are formed on the Pt surface [24, 25].

$$(CH_3OH)_{solution} \leftrightarrow Pt–(CO)_{ads} + 4H^+ + 4e^- \quad (1)$$

$$Pt–(CO)_{ads} + H_2O \leftrightarrow CO_2 + 2H^+ + 2e^- \quad (2)$$

At high potentials, the oxidation of Pt and formation of platinum oxides occurs which can lead to a decrease in the adsorption active sites available on the surface of the electrode and therefore, results in a decrease the peak current density (region III) [26,27]. In region IV, the reduction of platinum oxides to platinum and production of active sites take place, so the re-oxidation of the methanol molecules and methanol residues is carried out on the surface of the electrode, and a backward peak appears [28]. Finally, the catalyst surface poisoning leads to a decrease in current density (region V). The cyclic voltammograms of electrooxidation of methanol molecules on (a) Pt-Os/Clay/FTO, (b) Pt/Clay/FTO and (c) Pt/FTO in 0.3 M $HClO_4$ and 0.6 M methanol solution at a scan rate of 50 mV/s are shown in Fig. 3. It can be seen from this Figure that the values of the peak current densities for methanol oxidation at the Pt/FTO, Pt/Clay/FTO, and Pt-Os/Clay/FTO electrodes are equal to 2.69, 4.61, and 5.95 mA cm^{-2}, respectively. These results indicate that the Pt-Os/Clay/FTO electrode is more favorable for the methanol electrooxidation process, which is due to the presence of the clay distributed on the electrode surface. Furthermore, the clay film has a three-dimensional structure, and the incorporation of platinum nanoparticles into this porous clay [29, 30], makes it easier for the gaseous product to come out of the catalyst layer [31,32]. It is worth noting that the existence of the second metal particles in the catalyst and the synergistic effect in the two-component catalyst can improve the performance of the methanol electrooxidation process.

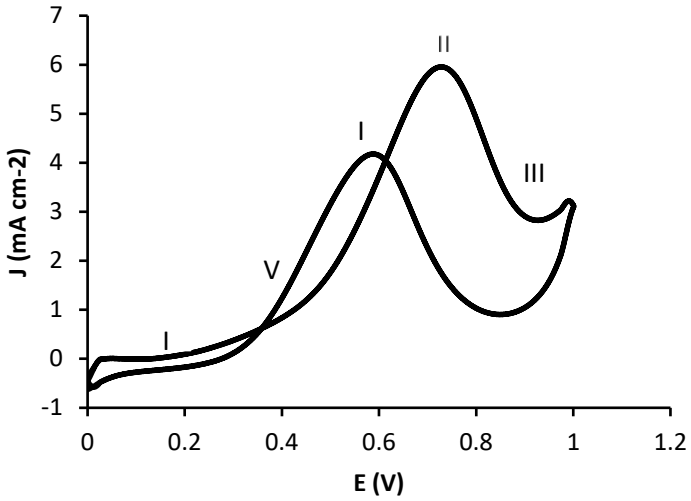

Figure 2. Cyclic voltammogram (CV) of methanol oxidation at the surface of Pt-Os/Clay/FTO in 0.3 M $HClO_4$ containing 0.6 M methanol at a scan rate of 50 mV s^{-1}

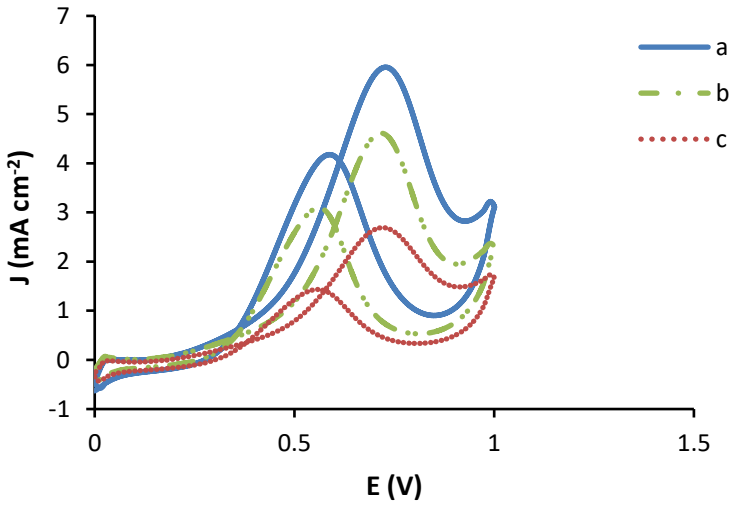

Figure 3. Cyclic voltammograms (CVs) of methanol oxidation at the surface of (a) Pt-Os/Clay/FTO, (b) Pt/Clay/FTO and (c) Pt/FTO in 0.3 M $HClO_4$ containing 0.6 M methanol at a scan rate of 50 mV s^{-1}

3.3. Electrochemical impedance spectroscopy (EIS) study

In electrochemical impedance spectroscopy measurement, the ohmic and the charge transfer resistance can be used to investigate the catalytic activity for the methanol electro-oxidation reaction on Pt-Os/Clay/FTO electrode. Figure 4, represents the Nyquist diagrams for methanol electrooxidation in 0.3 M $HClO_4$ containing 0.6 M methanol at room temperature. Table 1, shows the values of the equivalent circuit elements which are obtained by fitting the experimental results. As can be seen in Table 1, the modified Pt-Os/Clay/FTO electrode has a

lower charge transfer resistance compared to the Pt/Clay/FTO and Pt/FTO electrodes. This behavior is due to the homogenous dispersion of Pt and Os nanoparticles on to the montmorillonite clay layer. Therefore, the proposed Pt-Os/Clay composite can offer a most conductive surface for electrooxidation of methanol molecules in acidic solutions.

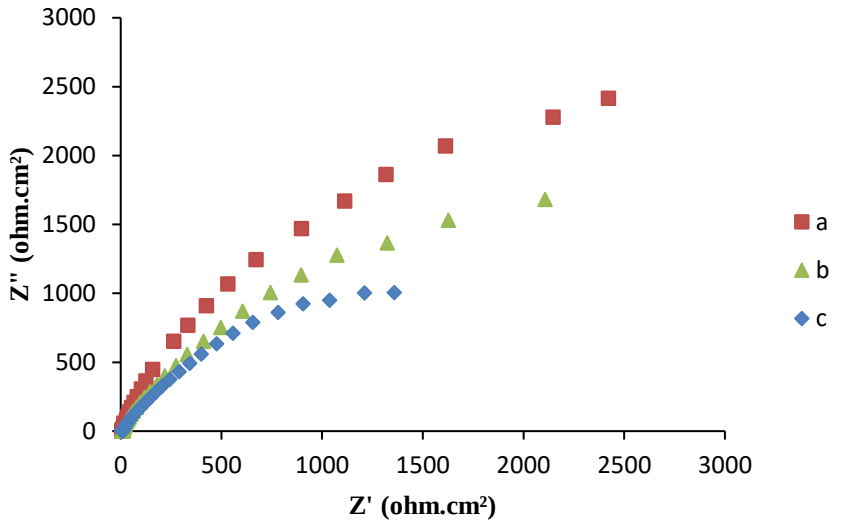

Figure 4. Nyquist plots of (a) Pt-Os/Clay/FTO, (b) Pt/Clay/FTO and (c) Pt/FTO electrodes in 0.3 M $HClO_4$ containing 0.6 M methanol

Table 1. The values of the equivalent circuit elements obtained by fitting the experimental results

Electrode	R_1(Ohm.cm^2)	R_2(Ohm.cm^2)	n	p
Pt/FTO	8.38	5799	0.7	0.00011
Pt/Clay/FTO	7.49	3964.3	0.81	0.00027
Pt-Os/Clay/FTO	7.81	2718.9	0.85	0.00015

3.4. Chronoamperometric studies

To investigate the electrocatalytic performance of the (a) Pt-Os/Clay/FTO, (b) Pt/Clay/FTO and (c) Pt/FTO electrodes for electrooxidation of methanol molecules, the chronoamperometry technique was employed. As is seen in Fig. 5, there is a gradual decay in the current density with the time and then followed by a relatively stable current at a longer time which can be explained by the poisoning of the Pt surface through the formation of the intermediate species [33]. Also, the oxidation current of the methanol molecules on the Pt-Os/Clay/FTO surface is higher than Pt/Clay/FTO and Pt/FTO electrodes. Due to the use of the two-component Pt-Os

catalyst and the regular dispersion of nanoparticles on the clay surface, the electrocatalytic activity of the Pt-Os/Clay/FTO is higher compared to the Pt/Clay/FTO and Pt/FTO electrodes.

It is also worth noting that the presence of a greater number of active sites on the Pt-Os/Clay/FTO surface can facilitate the electrooxidation of the methanol molecules. Therefore, the Pt-Os/Clay/FTO is a better electrode for long time operation.

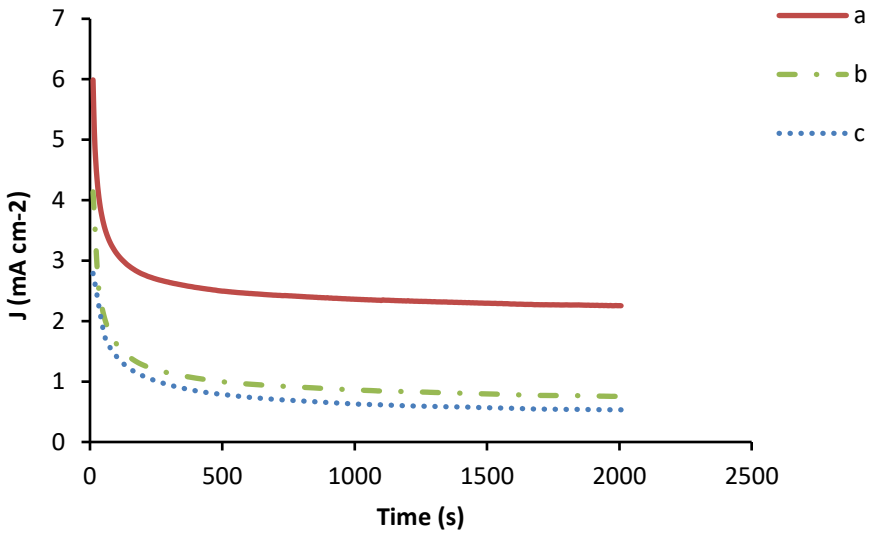

Figure 5. (A) Chronoamperograms of (a) Pt-Os/Clay/FTO, (b) Pt/Clay/FTO and (c) Pt/FTO in 0.3 M $HClO_4$ containing 0.6 M methanol

3.5. Effective parameters on the electrooxidation of methanol

3.5.1. Effect of MMT clay loading

To determine the optimum level of MMT clay as the modifier layer on the surface of the FTO electrode for methanol oxidation, serial experiments were performed. The effect of the amount of MMT on the anodic peak current density of methanol oxidation is shown in Fig. 6A. As is evident in this Figure, the current density increases progressively for the film thickness up to 20 µl and drops afterward. For MMT clay loadings lower 20 µl, the lamination of clay occurs and provides optimal three-dimensional areas for the catalyst. MMT clay loading in 20 µl has the optimum structure and porosity for the incorporation of metal nanoparticles. The decrease in the peak current densities beyond 20 µl may be due to the decrease in proton conductivity and the increase in silicate layers [34, 35], which leads to an increase in the proton transfer path. It seems that the 20 µl level of MMT clay can provide a better matrix for Pt and Os nanoparticle deposition. Therefore, 20 µl was chosen as an optimum level of MMT clay in the following experiments.

3.5.2. Effect of Electrochemical deposition time of platinum and osmium nanoparticles

The anodic peak current density of methanol electrooxidation, depends on the electrochemical deposition time of the nanoparticles on the MMT clay layer. A plot of the anodic peak current densities of Pt-Os/Clay/FTO as a function of the electrochemical deposition time of Pt and Os is shown in Fig. 6B.

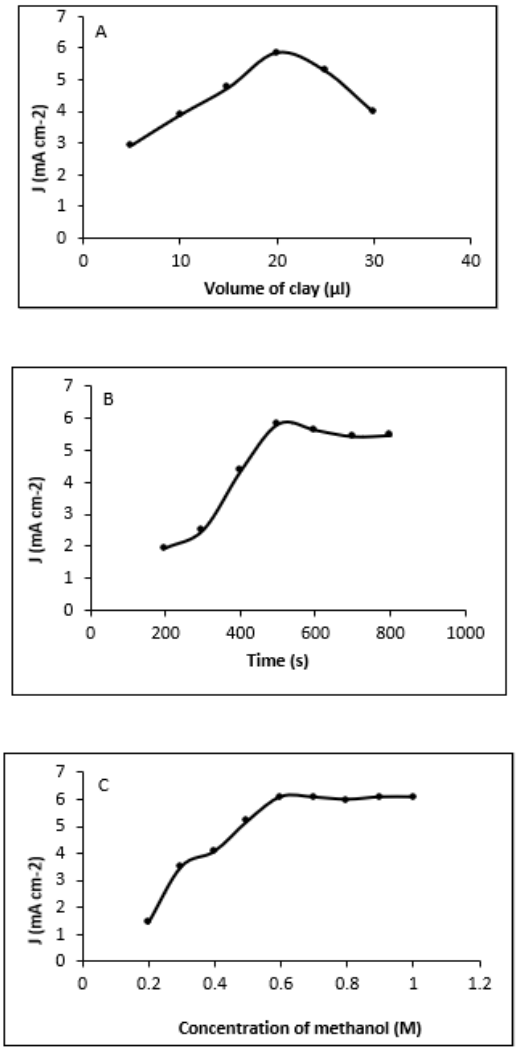

Figure 6. Effect of the (A) amount of MMT clay, (B) electrodeposition time of Pt-Os nanoparticles and (C)) methanol concentration on the oxidation peak current density of methanol

As can be seen in Fig. 6B, the anodic peak current densities of methanol electrooxidation increase with the increasing the electrochemical deposition time of Pt and Os from 200 to 500 s and then remain almost constant for the optimum time amount of 500 s. On the other hand, at the lower time, metal particles are almost uniformly deposited on the surface of the Clay/FTO electrode. However, any extra deposition time from 500s, does not increase the catalytic activity of the electrode, probably because of the increased metal particles agglomerate during the reduction process which results in a decrease of the electrochemically active area at the

surface of the fabricated electrode. Accordingly, because the anodic peak current densities did not increase significantly after 500 s, this time was considered as an optimum value.

3.5.3. Effect of methanol concentration

For further examination of the capacity of Pt-Os/Clay/FTO for electrooxidation of methanol molecules, the effect of methanol concentration on the corresponding oxidation current densities was investigated. The results are shown in Fig. 6C. As is evident in this Figure, the anodic peak current density increases with methanol concentration up to 0.6 M and then it reaches a nearly constant value. This effect is due to the saturation of the active sites at the surface of the electrode.

3.6. Electrochemical Characterization of Pt-Os/Clay/FTO

The electrochemical activity of the Pt-Os/Clay/FTO modified electrode, was studied by cyclic voltammetry in 0.5 M H_2SO_4, at a scan rate of 50 mVs^{-1}. Fig. 7, clearly shows the presence of three pairs of peaks. The oxidation and reduction peak couples (a/a´and b/b´) are related to desorption and adsorption of the hydrogen atoms on the electrode surface, and the another pair (c/c´) correspond to the formation and reduction of platinum oxide, respectively. In order to calculate the real surface area of the electrode (A_r), the measurement of the hydrogen adsorption is widely used [36]. The A_r value can be obtained by the following equation:

$A_r=Q_H/Q_o$

Q_H is the charge consumed for hydrogen adsorption and Q_o has been commonly taken as 0.21 $mC/realcm^2$ [37]. The roughness factor, R_f describes the enhancement of the real surface area (A_r) in comparison with the geometric area, A_g (cm^2):

$R_f = A_r/A_g$

Table 2. Physical characteristics of Pt/FTO, Pt/Clay/FTO and Pt-Os/Clay/FTO as determined from the charge corresponding to the hydrogen adsorption peaks in Fig. 6

Characteristics	**Electrode**		
	FTO /Pt	Clay/FTO/Pt	FTO/Clay/ Pt-Os
Pt loading	0.6	0.6	0.6
Q_o	0.21	0.21	0.21
Q_H	0.015	0.042	0.037
A_g	0.25	0.25	0.25
A_r	0.07	0.2	0.18
R_f	0.28	0.8	0.72

The physical characteristics for Pt/FTO, Pt/Clay/FTO, and Pt-Os/Clay/FTO constructed electrodes are given in Table 2. Based on the results reported in this Table, the real surface area of Pt/Clay/FTO is larger than the other electrodes. Therefore, the large surface area increases the catalytic activity of the electrode remarkably. The reduction of the real surface area of the Pt-Os/Clay/FTO relative to the Pt/Clay/FTO can be attributed to the successful formation of a bipolar alloy on the electrode surface.

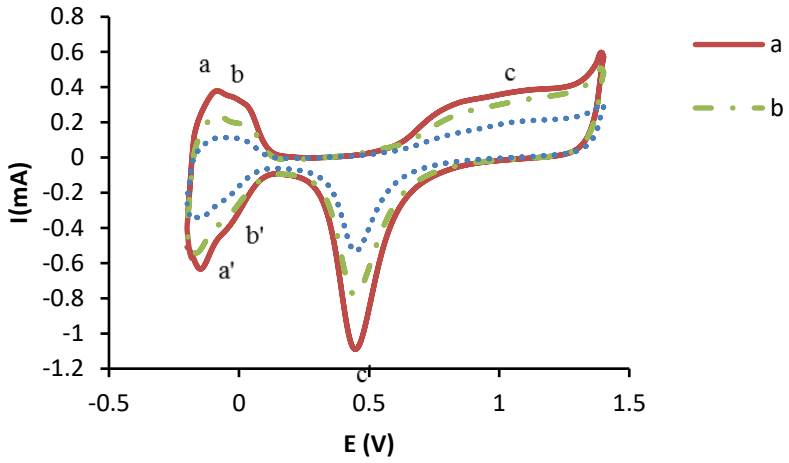

Figure 7. Cyclic voltammograms of (a) Pt-Os/Clay/FTO, (b) Pt/Clay/FTO and (c) Pt/FTO in 0.5 M H_2SO_4 solution at a scan rate of 50 mVs^{-1}

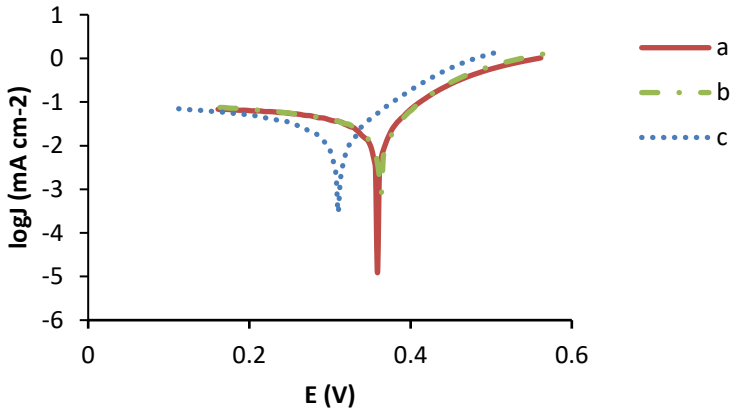

Figure 8. Tafel plots of (a) Pt-Os/Clay/FTO, (b) Pt/Clay/FTO and (c) Pt/FTO electrodes

3.7. Kinetic Analysis of methanol electrooxidation (Tafel plots studies)

The Tafel plots for evaluation of the electrocatalytic activity of the electrodes are shown in Figure 8. The values of exchange current densities (J_o) were determined for Pt/FTO (2.48×10^{-6} mA cm^{-2}), Pt/Clay/FTO (4.01×10^{-6} mA cm^{-2}) and Pt-Os/Clay/FTO (8.45×10^{-6} mA cm^{-2}) from the Tafel plots. It is seen that the exchange current density of the Pt-Os/Clay/FTO electrode is

higher than the other electrodes. It is worth mentioning that the methanol electrooxidation at the Pt-Os/Clay/FTO electrode surface is less limited kinetically.

3.8. Catalytic efficiency

The catalytic efficiency of the electrooxidation process of the methanol molecules is sensitive to the electrode substrate. To select a suitable substrate, the gold, platinum and glass carbon electrodes were modified with the optimal amount of clay and platinum and osmium nanoparticles and the cyclic voltammograms were recorded on the surface of these electrodes. Figure 9, shows the corresponding CVs for electrooxidation of methanol molecules in 0.3 M $HClO_4$ containing 0.6 M methanol at a scan rate of 50 mVs^{-1}. As is presented in Fig. 9, the Pt-Os/Clay/FTO electrode has a higher current density for methanol electrooxidation than the other electrodes. Therefore, FTO was selected as a suitable substrate for the stabilization of clay and platinum and osmium nanoparticles.

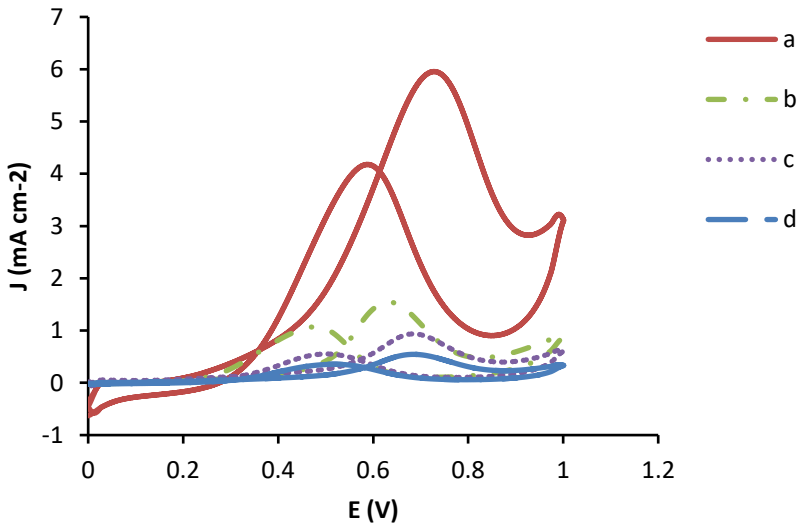

Figure 9. Comparison of the anodic peak current density for methanol oxidation at the surface of (a) Pt-Os/Clay/FTO, (b) Pt-Os/Clay/PtE, (c) Pt-Os/Clay/AuE and (d) Pt-Os/Clay/GCE

3.9. Comparison of electrocatalytic activity of Pt-Os/Clay/FTO with some modified electrodes

Finally, the electrocatalytic activity of the prepared electrocatalyst was compared with some recently reported Pt-modified electrodes in Table 3. The ratio of forwarding current to backward current (I_{pf}/I_{pb}) is the parameter that can be used to evaluate the catalyst tolerance to poisoning [38]. As is evident in Table 3, the Pt-Os/Clay/FTO has a better and comparable electrochemical characteristic than the other modified Pt-electrodes and can exhibit a considerable condition for methanol electrooxidation in solutions. The notable enhancement in

the ratio of the forwarding current to the backward current, can be ascribed to the disposable nature of the FTO substrate which increases the tolerance of the electrode surface to the poisoning effect.

Table 3. Comparison of the electrocatalytic activity of Pt-Os/Clay/FTO with some recently reported Pt-modified electrodes

Number	Modified electrode	I_b/ I_f	Reference
1	Pt/CCG	0.72	[39]
2	PtNWNs/C	0.96	[40]
3	GNP/Pt	1.21	[41]
4	Pt/graphene	1.071	[42]
5	Pt/T-NFs	1.01	[43]
6	Pt-Os/Clay/FTO	1.44	This work

4. CONCLUSION

In this research work, a FTO electrode modified with montmorillonite (MMT) clay and platinum-osmium (Pt-Os) bimetallic nanoparticles was constructed for methanol electrooxidation. The Pt-Os/Clay/FTO electrode was characterized by SEM and EDX techniques. The cyclic voltammetry and chronoamperometry techniques were used to study the electrocatalytic activity of the proposed Pt-Os/Clay/FTO electrode for the methanol electrooxidation. The electrochemical results showed that the catalytic activity of Pt-Os/Clay/FTO is better compared to the other fabricated electrodes used in this study. It seems that the enhanced electrocatalytic properties of the modified electrode may be due to the synergistic effects of the MMT clay and nanoparticles and the high dispersion of the platinum and osmium nanoparticles on the clay film. The effect of different parameters such as MMT clay loading, electrochemical deposition time of platinum and osmium nanoparticles and the methanol concentration on the performance of the developed electrode and the enhancement of the anodic peak current of the methanol molecules electrooxidation was studied. Moreover, in comparison to the other substrates, the catalytic activity of MMT clay and Pt-Os nanoparticles on the FTO electrode surface, was better than the electrocatalytic activities which are reported for the other fabricated electrodes.

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