*Int. J. Electrochem. Sci.*, 7 **(2012)** 768 - 784

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

# Graphene Supported-Pt-M (M = Ru or Pd) for Electrocatalytic Methanol Oxidation

*Ahmed Galal, Nada F. Atta*[*], *Hagar K. Hassan*

Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt
[*]E-mail: nada_fah1@yahoo.com

*Received:* 1 November 2011 / *Accepted:* 11 December 2011 / *Published:* 1 January 2012

Different methods for preparation of a highly efficient catalyst made of a hybrid of graphene and sub-micron structured Pt-Ru or Pt-Pd is illustrated for methanol oxidation. Graphene is prepared chemically using microwave method or electrochemically by reducing graphene oxide (GO). Glassy carbon (GC) electrodes are modified with the catalyst. The electrocatalytic activity of the surface is examined for methanol oxidation with cyclic voltammetry (CV), chronoamperometry (CA) and chronocoulometry (CC). The electrocatalytic activity is doubled when graphene is modified with Pt-Pd and increases five times in case of Pt-Ru compared to GC - Pt-Pd and Pt-Ru electrodes, respectively. SEM and AFM are used to characterize the catalyst morphology and surface roughness of the catalyst. Effect of catalyst loading, temperature, stability, and methanol concentration on the catalyst efficiency are presented.

**Keywords:** Graphene; Electrocatalysis; Composite Electrodes; methanol oxidation; AFM; SEM.

## 1. INTRODUCTION

Among the different types of supports used in heterogeneous catalysis carbon materials attract a growing interest due to their specific characteristics which are mainly: (i) resistance to acid/basic media, (ii) possibility to control, up to certain limits, the porosity and surface chemistry and (iii) easy recovery of precious metals by support burning resulting in a low environmental impact [1]. It is observed that the structures and properties of carbon support, such as surface function groups [2], graphitization structure [3,4], and surface area [5] have a large effect on the activity of the catalyst, so they attracted a numerous interests in recent years in many fields, such as capacitor, catalyst or fuel cells and batteries [6]. Various carbon allotropes, including graphite, diamond, fullerenes, and carbon nanotubes (CNTs), have very different electrochemical properties from each other [7]. Graphene was the missing allotrope of pure carbon materials. Graphene is a member of 2-dimentional materials discovered by Andre Geim's research group at University of Manchester in 2004, it is one atom thick that consists of a hexagonal array of $Sp^2$- bonded carbon atoms [8,9] looks like a honey comb [8,10,11]. Single walled nanotubes (SWCNTs) can be viewed as the result of rolling up a sheet of graphene [6, 16]. Graphene has some unique properties which make it one of the most interesting materials nowadays even compared to CNTs. such as has large theoretical surface area about 2620 $m^2/g$ [11,15,6], chemically stable and almost impermeable to gases, can withstand large current densities, has high thermal [7] and chemical conductivity [12-14], has outstanding mechanical properties [13,14], has large amount of edge planes/defects[12], in addition to its cheap production cost compared to CNTs [14]. All of these properties make it promising for potential application in electrochemical field [12] and represents a promising catalyst carrier in the next generation of carbon based support [14].

The electrochemical oxidation of small organic molecules such as methanol, formic acid, and formaldehyde has been the field of intensive research for the development of direct fuel cell [17].The high activity of methanol oxidation on platinum makes this metal a suitable electro-catalyst for the DMFCs anode [20] where platinum is known to activate the dissociative adsorption of methanol at an appreciable rate [19]. However, during this process, CO, formaldehyde, formic acid and other intermediate organic compounds are produced which act as a poison to the platinum catalyst [17, 18, 21, and 22]. Accompanying platinum with other metals such as ruthenium [18, 23, and 24] or palladium [18] could improve the activity of the catalyst by removing the adsorbed CO intermediates from platinum. In addition to both ruthenium and palladium are relatively much cheaper than platinum.

In this work different method was proposed for preparation of co-catalyst graphene sub-micron composite where graphene was prepared chemically using microwave method and Pt, Pt-Pd and Pt-Ru were deposited on graphene sheets and their electrocatalytic activity for methanol oxidation were investigated. Several experiments such as effect of catalyst loading, effect of temperature, effect of methanol oxidation, effect of scan rate, Chronoamperometry (CA), Chronocoulometry (CC), and long term stability were carried out. Graphene was prepared also via electrochemical method and a comparison between chemically converted graphene and electrically converted graphene was performed.

## 2. EXPERIMENTAL

### *2.1 Chemicals and Materials.*

All chemicals were used as received without further purification. Graphite powder, perchloric acid, sulfuric acid, nitric acid, hydrochloric acid, and methanol, (Sigma Aldrich). Hydrazine hydrate, hexachloroplatinic acid (Aldrich). Palladium (II) chloride (Fluka) and ruthenium (III) chloride (fluka).

### *2.2 Preparation of Graphene Oxide (GO).*

Graphene oxide (GO) was prepared by oxidation of high purity graphite powder according to the method of Hummer and Offeman [25] with some modifications; Stirring about 1 g of graphite powder (spectroscopic grade) and 0.525 g of sodium nitrate into 24 ml of $66^{\mathbf{0}}$ Be technical sulfuric acid (93% $H_2SO_4$). The ingredients were mixed and cooled to 0 $^0$C in an ice-bath as a safety measure. While maintaining vigorous agitation, 5.0 g of potassium permanganate was added to the suspension. The rate of addition was controlled carefully to prevent the temperature of the suspension from exceeding 20 $^0$C. The ice-bath was then removed and the temperature of the suspension is brought to 35 ± 3 $^0$C**,** where it was maintained for 90 minutes. Water (48 ml) was slowly stirred into the paste, causing violent effervescence and an increase in temperature to 98 $^0$C. The diluted suspension, brown in color, was maintained at this temperature for 15 minutes. The suspension was then further diluted to approximately 150 ml with warm water and treated with 3% hydrogen peroxide to reduce the residual permanganate and manganese dioxide into colorless soluble manganese sulfate. Upon treatment with the peroxide, the suspension turned bright yellow. The suspension was filtered resulting in a yellow-brown filter cake while maintaining the suspension warm during filtration to avoid precipitation of mellitic acid formed as a side reaction then the suspension was washed three times with warm water and dried in air.

### *2.3 Preparation of Graphene.*

#### *2.3.1 Preparation of graphene by chemical reduction of GO.*

Graphene was prepared by reduction of GO using microwave method in presence of hydrazine hydrate (HH) as reducing agent [26] where, 0.1 g of GO was sonicated with 20 ml of deionized water until a homogeneous yellow dispersion was obtained where GO can be dispersed easily in water due to presence of a variety of hydrophilic oxygen groups (OH, O, COOH). After adding 120 μl of HH, the solution was placed in a conventional microwave oven (MC-9283 JLR, 900 W) and operated at a full power 900 W in 30 s cycles ( on for 10 s, off and stirring for 20 s) for a total reaction time of 120 sec.

After microwave irradiation the yellow color of solution was converted into black that indicates the complete reduction of GO into CCG. the graphene flakes were separated by Mark IV auto bench centrifuge operated at 5000 rpm for 15 min and dried overnight.

#### *2.3.2 Preparation of Graphene by Electrochemical Reduction of GO.*

Graphene oxide (1.5 mg) was dispersed in 1 ml of deionized water and sonicated for 2 h. Of this homogeneous solution, 10 μl was pipetted on the surface of well-polished GC electrode after activation in 0.5 M $H_2SO_4$ by cyclic voltammetry from -500 mV to 1500 mV for 5 cycles and left to dry at room temperature.

GO was dried on the surface of GC electrode and followed by electrochemical reduction by bulk electrolysis (BE) at -1200 mV for 15 minutes  using three electrode system, 4 M Ag/AgCl as reference electrode, Pt wire as counter electrode and GC/GO as working electrode in 0.5 M NaCl solution as electrolyte.

### 2.4 Preparation of Catalysts Solution.

Preparation of Platinum–Palladium (Pt-Pd) catalyst was prepared by dissolving $H_2PtCl_6$ and $PdCl_2$ (equivalent to ratio 3 Pt: 1Pd) in aqua regia. The formed solution was heated until one-fourth of the original volume was reached by evaporation. The remaining solution was diluted to the required volume and concentration by 0.1M perchloric acid. While, platinum or platinum- Ruthenium (Pt-Ru) was prepared by dissolving $H_2PtCl_6$ in 0.5M $H_2SO_4$ or $H_2PtCl_6$ and $RuCl_3$ to prepare Pt-Ru solution with ratio 3Pt:1Ru with the required volume and concentration. These solutions were used to prepare the mixed co-catalyst as will be discussed later.

### 2.5 Electrochemical Cells and Equipments.

Electrochemical experiments were carried out in a three electrode /one compartment glass cell. The working electrode was GC electrode (diameter: 3mm), reference electrode was 4M Ag/AgCl and Pt wire as Auxiliary electrode. GC electrode was polished using (2 µm)/water slurry until no observed scratches were observed. Cyclic Voltammetry (CV) experiments were performed using Volta lab (PGZ 301), Chronoamperometry (CA) and Chronocoulometry (CC) were performed using BASi EPSILON.

### 2.6 Preparation of Electrode for Electrochemical Measurements.

1 ml of DMF was added to 1.5 mg of CCG and was sonicated until a homogeneous suspension was obtained. GC electrode was polished well, rinsed with distilled water and casted with suitable volume of CCG suspension (5 µl). The electrode with CCG was left to dry for about 2h. The surface became ready for electro-deposition of catalyst and co-catalysts which can be performed by CV in three electrodes, one-compartment cell using the catalyst or co-catalyst solutions as electrolyte. Deposition of Pt and Pt-Pd was performed by applying potential from -250 mV to +650 mV Vs. 4M Ag/AgCl reference electrode at scan rate 50 mV/Sec for 30 cycles, while in case of Pt-Ru the CV was performed by applying potential from -1000 mV to 0 V Vs. 4M Ag/AgCl reference electrode at scan rate 50 mV/Sec for 15 cycles.

### 2.7 Surface Characterization.

Thin film XRD was recorded on Panlytical X`Pert using Cu-Kα radiation (λ = 1.540 Ǻ), FE-SEM by JEOL JSM-6360LA and Philips XL30, AFM by Shimadzu Wet – SPM (Scanning Probe microscope).

## 3. RESULTS AND DISCUSSIONS

### 3.1 Structural and Surface Characterizations.

The morphology of the CCG and ECG on glassy carbon sheet (the film prepared on GC sheet is the same as that prepared on the GC electrode surface) was characterized by FE-SEM and typical images are shown in Figures 1a and 1b, respectively. The micrographs show that chemically converted graphene sheet are rippled and crumpled with a dimension of several nm to few µm while ECG is more homogeneous and more compact on the surface than CCG. FE-SEM images and the corresponding EDAX analyses of CCG/Pt-Pd and CCG/Pt-Ru are shown in Figures 1c, 1d and 2 respectively which indicate the good dispersion of both Pt-Pd and Pt-Ru on CCG. Atomic force microscope was also used to investigate the structure of CCG, ECG, Pt-Pd and Pt-Ru supported on Graphene and the typical 3D images are shown in Figure 3. It is clear that ECG is more homogeneous than CCG although they have nearly the same roughness factor 1.63 and 1.67 respectively. The roughness factor and average particle size of both CCG/Pt-Pd and CCG/Pt-Ru are 1.594, 1.43 and 233 nm, 152 nm respectively**.**

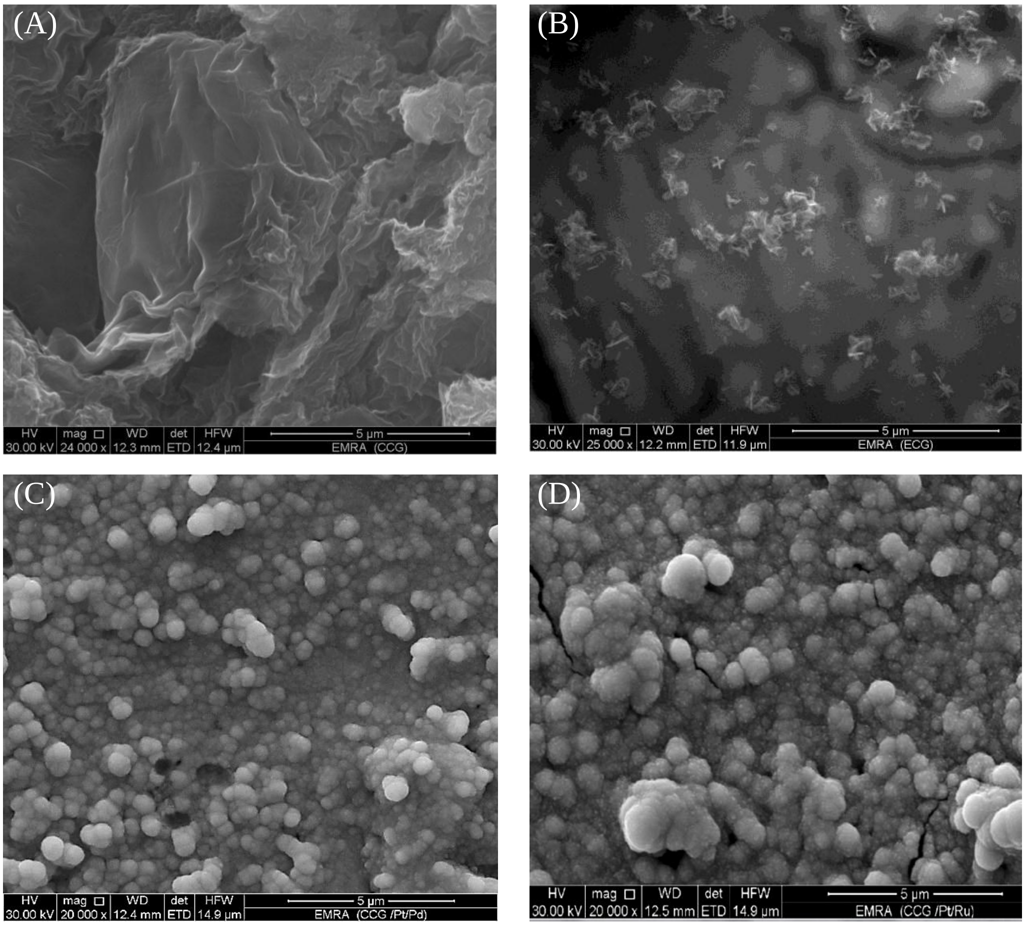


**Figure 1.** SEM images using FE-SEM for a**)** CCG, b) ECG, c) CCG/Pt-Pd and d) CCG/Pt-Ru.

### *3.2 Electrocatalytic Activity toward Methanol Oxidation.*

The electrocatalytic oxidation of methanol on graphene supported Pt, Pt-Pd and Pt-Ru sub-micron particles was characterized by cyclic voltammetry in 0.5M $CH_3OH$ and 0.1M $H_2SO_4$ from -500 to 1500 mV at 50 mV/s. The voltammogram was repeated until stable and reproducible CV curve was obtained. Figure 4 shows the cyclic voltammograms of different surfaces modified with different catalysts Pt, Pt-Pd and Pt-Ru. The substrates used were glassy carbon (GC) and glassy carbon/chemically converted graphene (GC/CCG). It is shown that the presence of graphene as a substrate increases the peak current from two to five times as compared to GC modified surfaces. Graphene itself has no catalytic activity in methanol where it does not give any peak during oxidation of methanol when it is used without any modifications with catalyst or co-catalyst. Two peaks corresponding to methanol oxidation can be identified in the potential range between +300 to +1200 mV, the oxidation peak in the forward direction refer to the oxidation of methanol and the oxidation peak in the reverse direction associated with the removal of CO and other residual carbon species formed at the electrode surface on the forward sweep.

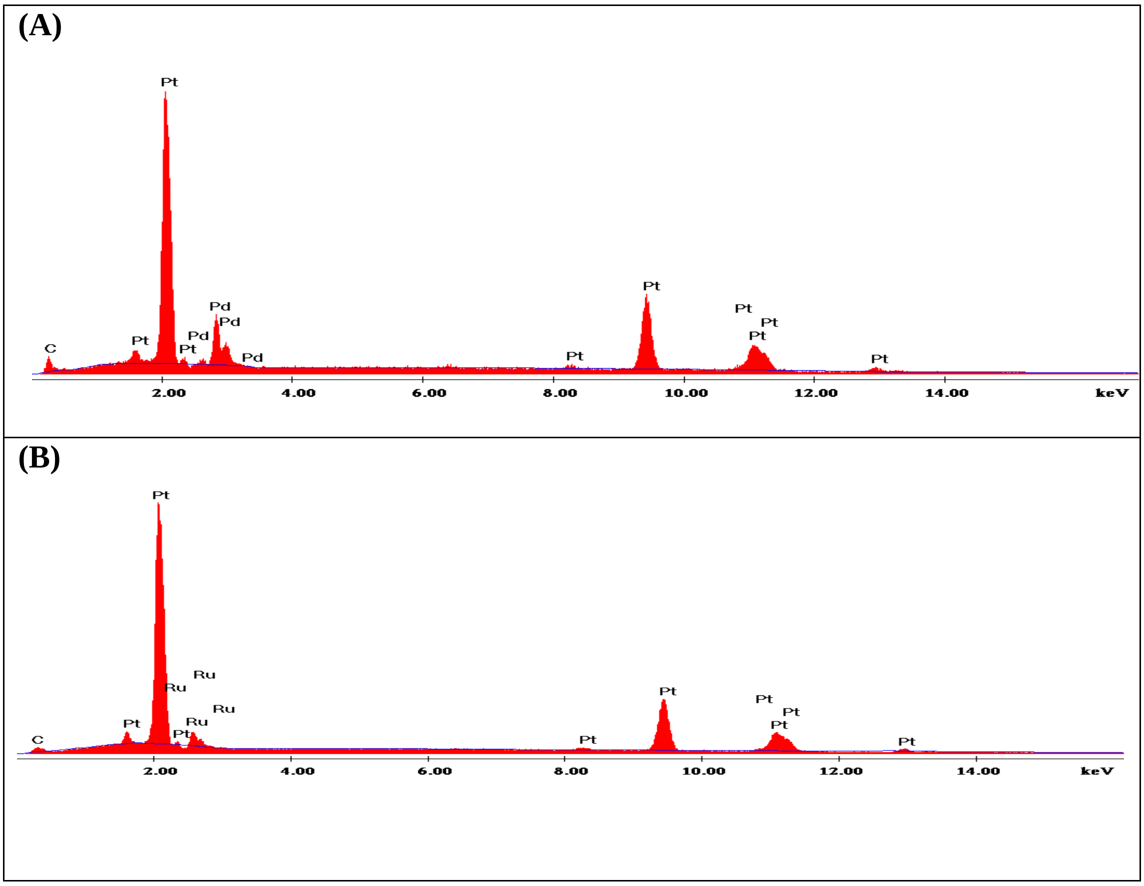


**Figure 2.** EDAX analyses for (A) CCG/Pt-Pd and (A) CCG/Pt-Ru**.**

The position of oxidation potential changes according to: the type of both the substrate and the deposited catalyst or co-catalyst. Graphene supported Pt-Ru sub-micron particles have a higher activity in methanol oxidation even at relatively lower loading when compared to Pt-Pd sub-micron particles. The current response recorded in the oxidation process was in the order of GC/CCG/Pt-Ru > GC/CCG/Pt-Pd > GC/Pt-Pd > GC/Pt-Ru. It is observed that presence of graphene enhances the electrocatalytic activity compared to GC/Pt-Ru or GC/Pt-Pd. This is probably due to the high surface area of graphene which leads to increase in the dispersion of Pt-Ru on its surface; hence the surface area of the electrode increases. The results show that GC/CCG/Pt-Ru gives higher peak current than GC/CCG/Pt-Pd in spite the fact that loading of Pt-Pd was nearly twice that of Pt-Ru. The reason for the high potential of methanol oxidation when using graphene as a substrate is due to residual oxygen containing functional groups on the surface [28]. Both Pd and Ru have no contribution in methanol oxidation but they provide sites for adsorption of oxygenated species $(OH)_{ads}$ which contributes in oxidation of Pt $(CO)_{ads}$. Therefore, Pd and Ru are favorable for removing the adsorbed CO intermediates from Pt, which are formed during methanol oxidation and thus poison the catalysts that leads to reduction in the activity for methanol oxidation reaction. From the previous results we conclude that Ru has higher ability for preventing the poisoning of Pt than Pd when using graphene that also provide higher additional sites for adsorption of oxygenated species.

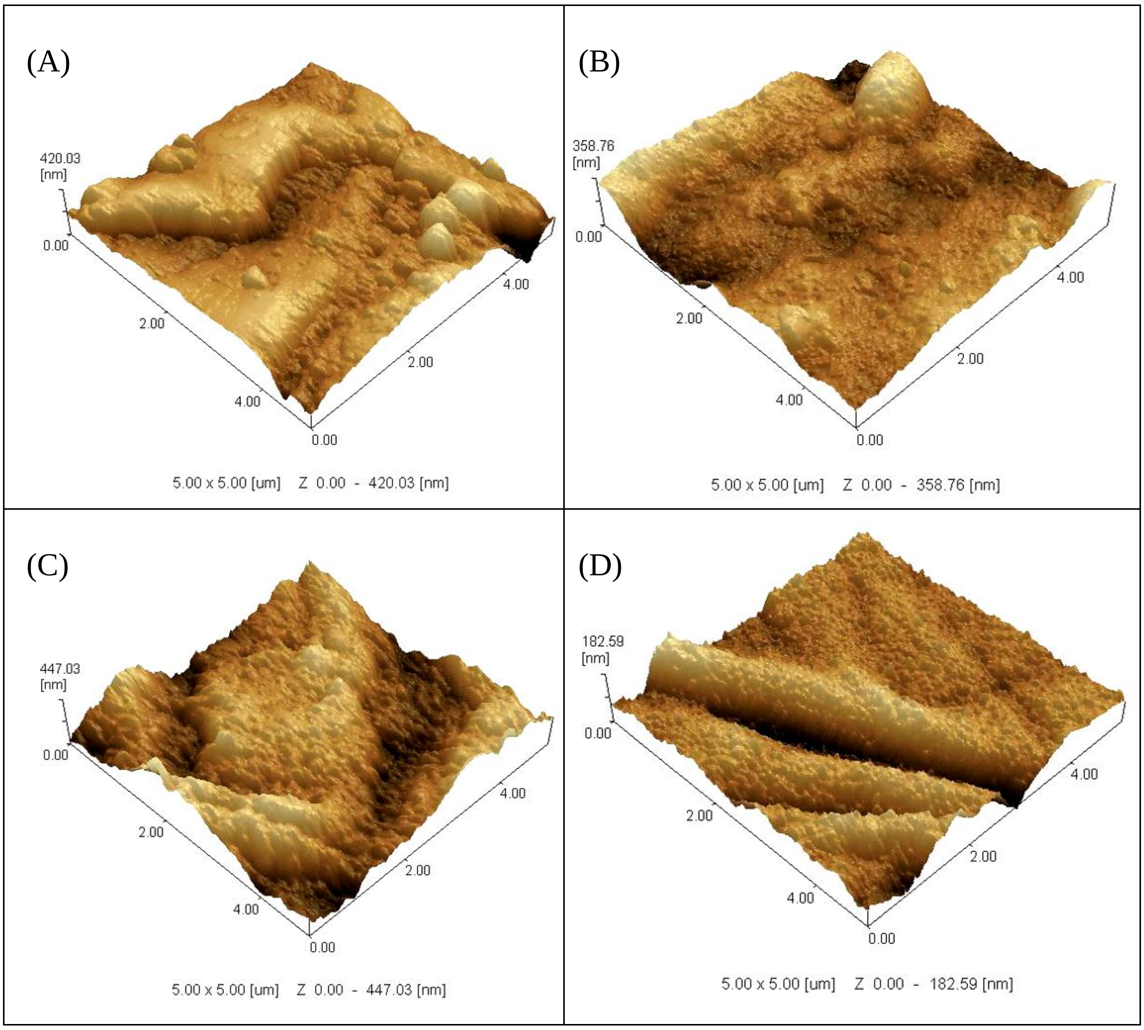


**Figure 3.** 3D-AFM images for a) CCG, b) ECG, c) CCG/Pt-Pd and d) CCG/Pt-Ru**.**

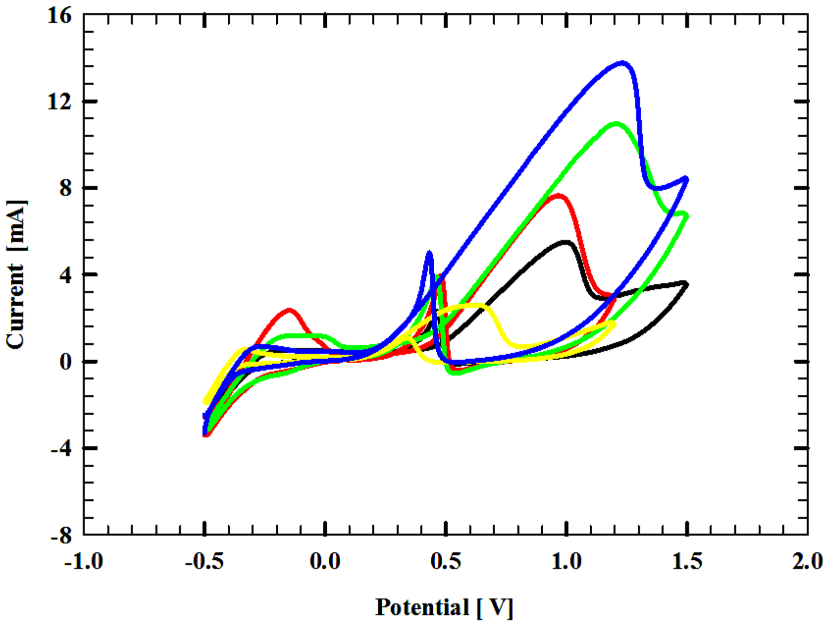


**Figure 4.** Cyclic voltammetry of methanol oxidation using different surfaces , —GC/G/Pt, — GC/Pt+Pd(3:1), —GC/G/Pt+Pd(3:1), — GC/Pt+Ru (3:1) and — GC/G/Pt+Ru (3:1), where deposition of Pt and Pt+Pd is by 30 cycles CV, deposition of Pt+Ru is by 15 cycles CV.

### *3.3 Effect of Co-catalysts Loading.*

The effect of changing co-catalyst loading by changing the number of cycles on electrocatalytic properties was also studied. In Figure 5 the results show that as the number of repeated cycles during Pt-Pd deposition increases the anodic peak current of methanol oxidation increases and the oxidation potential shift to more positive value up to 30 cycles after that the anodic peak current and potential become nearly stable, while in case of Pt-Ru the anodic peak current increases as number of deposition cycles increases giving a straight line by plotting anodic peak current versus number of cycles. CVs for them are present in supplementary 1 and 2.

### *3.4 Electrochemical Stability.*

Long-term stability for GC/CCG/Pt-Pd and GC/CCG/Pt-Ru was carried out along 8 days and the electrocatalytic activity of the electrode by cyclic voltammetry in 0.5M $CH_3OH$+0.1M $H_2SO_4$ was determined each 2 days, the voltammogram was repeated until reproducible CV was obtained. In Figure 6 the results indicate that GC/CCG/Pt-Ru has higher stability than GC/CCG/Pt-Pd. Thus, GC/CCG/Pt-Ru showed 23% decrease in current after 8 days compared with 32% decrease in current for GC/CCG/Pt-Pd which emphasizes the preference of using ruthenium.

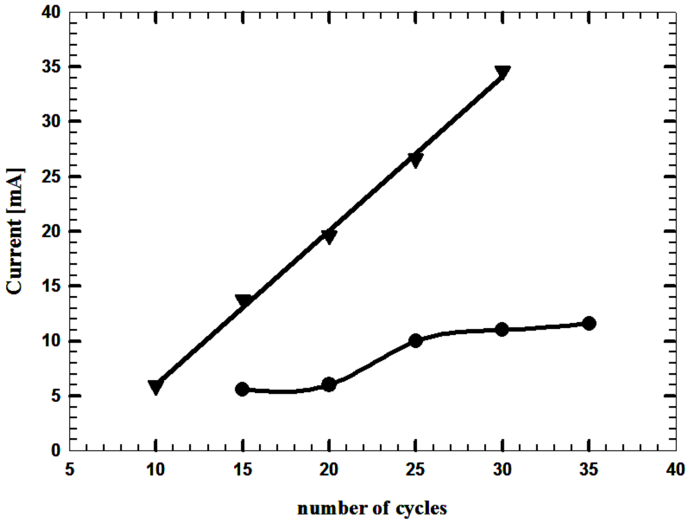


**Figure 5.** Effect of co-catalyst loading on electrocatalytic activity of methanol oxidation at –●– GC/G/Pt-Pd (3:1) and –▼– GC/G/Pt-Ru (3:1) in 0.5M $CH_3OH$ + 0.1M $H_2SO_4$.

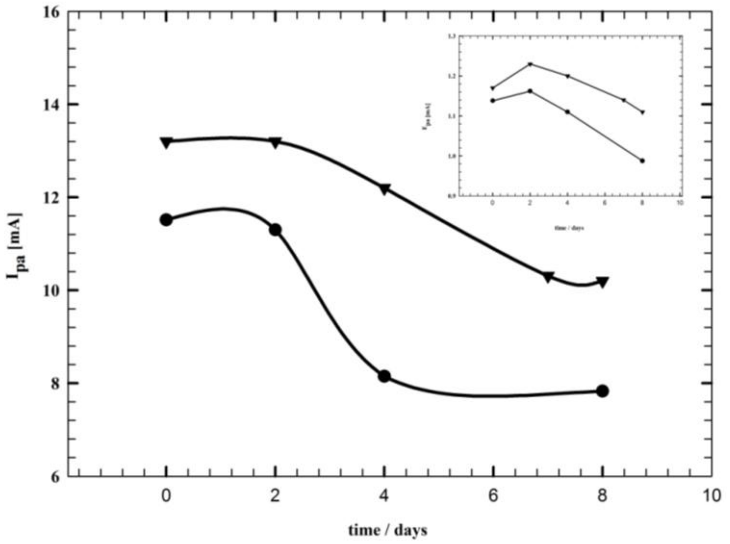


**Figure 6.** The variation of peak current (major), and peak potential (minor ) with time along 8 days for –●– GC/G/Pt-Pd (3:1) and –▼– GC/G/Pt-Ru (3:1) in 0.5M MeOH + 0.1M $H_2SO_4$.

### *3.5 Determination of Diffusion Coefficients.*

The forward oxidation current is proportional to the square root of the scan rate, suggesting that the oxidation behavior of methanol is controlled by diffusion process as shown in Figure 7. Diffusion coefficients of methanol at GC/CCG/Pt-Pd, and GC/CCG/Pt-Ru are calculated using different techniques cyclic voltammetry (CV), chronoamperometry (CA) and chronocoulometry (CC). The results are summarized in Table 1 which provide a comparable diffusion coefficient values for both electrodes but diffusion coefficient in case of GC/CCG/Pt-Ru is slightly higher than diffusion coefficient in case of GC/CCG/Pt-Pd which indicates faster diffusion process of methanol at the surface of GC/CCG/Pt-Ru.

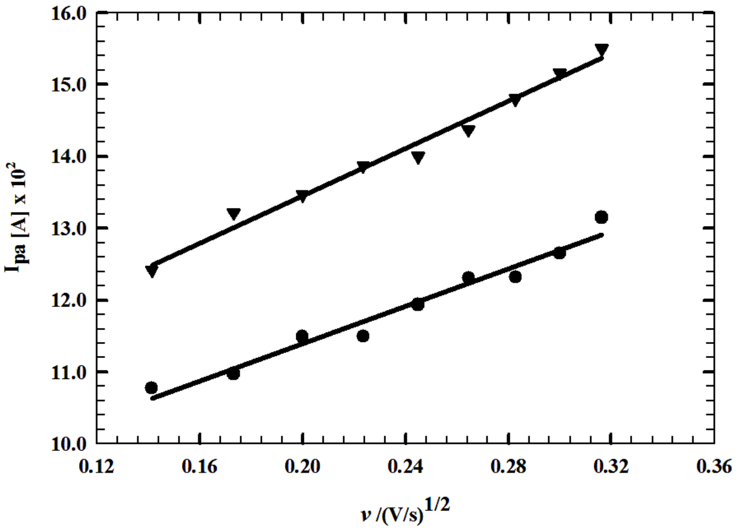


**Figure 7.** Effect of scan rate –●– GC/G/Pt-Pd (3:1) and –▼– GC/G/Pt-Ru (3:1) in 0.5M MeOH + 0.1M $H_2SO_4$.

**Table 1.** Diffusion coefficients of GC/CCG/Pt-Pd and GC/CCG/Pt-Ru in 0.5M$CH_3OH$+ 0.1M $H_2SO_4$ using different electrochemical techniques.

| Technique | GC/G/Pt-Pd | GC/G/Pt-Ru |
|---|---|---|
| CA | 0.464 × $10^{-6}$ $cm^2$/sec | 0.533 × $10^{-6}$ $cm^2$/sec. |
| CC | 0.67 × $10^{-6}$ $cm^2$/sec. | 0.92 × $10^{-6}$ $cm^2$/sec. |
| CV | 3.59 × $10^{-6}$ $cm^2$/sec. | 1.95 × $10^{-6}$$cm^2$/sec. |

### *3.6 Effect of Temperature.*

Effect of temperature changes [20-60 $^oC$] at GC/CCG/Pt-Ru and GC/CCG/Pt-Pd in 0.5M $CH_3OH$ + 0.1M $H_2SO_4$ is shown in Figure 8a. In case of GC/CCG/Pt-Pd the maximum current was obtained for working temperature 30 $^0C$ then decreases and becomes nearly stable. On the other hand, GC/CCG/Pt-Ru does not show this trend where the peak current increases as the temperature increases which indicates that the mechanism of methanol oxidation at the surface of GC/CCG/Pt-Ru may be only activation controlled. However, in case of GC/CCG/Pt-Pd the mechanism of methanol oxidation is activation controlled at lower temperature but at higher temperature the adsorption of methanol becomes the rate determining step as indicated from the current that decreases with temperature. By plotting log $I_{pa}$ (anodic peak current) versus reciprocal of temperature we can calculate the value of activation energy $E_a$ as indicated in Figure 8b The results show that $E_a$ using GC/CCG/Pt-Ru = 4.4 KJ/mol., while Ea using GC/CCG/Pt-Pd = 9.2 KJ/mol. This result explains the higher electrocatalytic behavior of GC/CCG/Pt-Ru compared to GC/CCG/Pt-Pd.

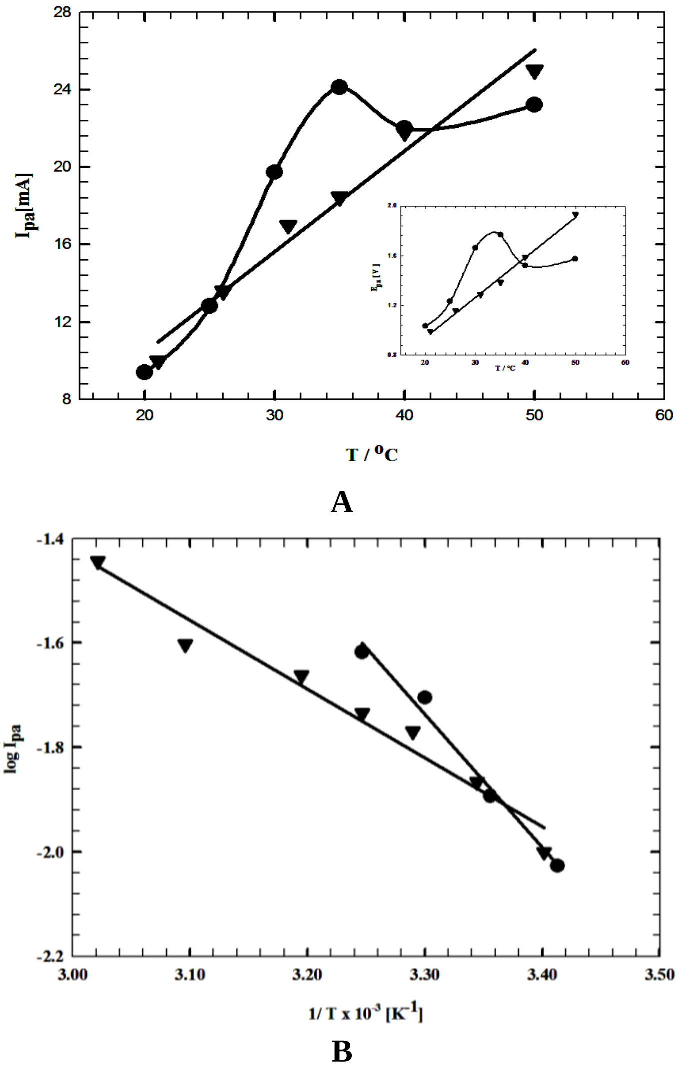


**Figure 8.** (A) Change in peak current and peak potential (inset) with changing the temperature on methanol oxidation and (B) Arrhenius plot between $I_{pa}$ versus 1/ T K, –▼–GC/G/Pt+Ru(3:1) and –●–GC/G/Pt+Pd(3:1) in 0.5M MeOH+0.1M $H_2SO_4$..

### *3.8 Effect of Methanol Concentration.*

On the other hand, as the concentration of methanol increases both the oxidation peak in the forward scan and oxidation peak in the reverse scan increase. The dependence of peak current on the concentration of methanol ranging from 0.5 M to 3 M using both electrodes GC/CCG/Pt-Ru and GC/CCG/Pt-Pd is shown in Figure 9. The results show that the current response for GC/CCG/Pt-Pd reaches steady state at high concentration of methanol while in case of GC/CCG/Pt-Ru linear relationship is obtained by plotting anodic peak current versus concentration and as the methanol concentration increases the anodic peak current increases. All of these results imply that GC/CCG/Pt-Ru resists the accumulation of electro-oxidation products more than GC/CCG/Pt-Pd. CVs for both GC/CCG/Pt-Ru and GC/CCG/Pt-Pd in different methanol concentrations are shown in supplementary 3 and 4.

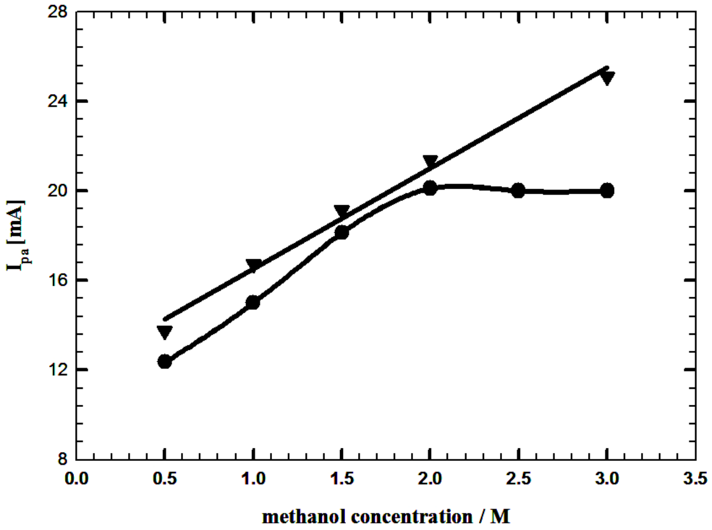


**Figure 9.** The variation of peak current with methanol concentration –●– GC/G/Pt-Pd (3:1) and –▼– GC/G/Pt-Ru (3:1) in different concentration of MeOH + 0.1M $H_2SO_4$.

### *3.10 Electrochemically Reduction of GO to Form ECG.*

Chemical and thermal reduction techniques have some obvious drawbacks, namely, the highly toxic reductant hydrazine and the incompatibility of the thermal reduction process under some conditions [28]. Thus, the electrochemical method was adopted as an effective controllable and alternative technique for the modification of electronic states. This is done by adjusting the external power source to change the Fermi energy level of the electrode surface [29], which reduces GO in the presence of direct current (DC) bias [30]. A comparison between CCG and ECG was carried out by cyclic voltammetry in 0.5M $CH_3OH$ + 0.1M $H_2SO_4$ from -500 to +1500 mV, scan rate 50 mV/s using Pt-Pd and Pt-Ru co-catalysts as shown in Figure 10. The results indicate that ECG substrate gives comparable electrochemical activity to CCG. The thickness of ECG can be controlled by adjusting the concentration of the GO colloid solution and reduction time. Figure 11a shows the cyclic voltammetry of GC/EGC/Pt-Pd in 0.5M $CH_3OH$ +0.1M $H_2SO_4$ at different reduction times of GO from 10 to 25 minute. The results indicate higher electrochemical activity for thinner thickness of ECG where 10 min was not enough time for reduction of GO at this potential. Figure 11b shows the cyclic voltammetry of GC/EGC/Pt-Pd in 0.5M $CH_3OH$ +0.1M $H_2SO_4$ at different reduction potential for reduction of GO into ECG, the results predicted that -1200 mV is the optimum reduction potential and by increasing the potential unpredicted decreasing in anodic current of methanol oxidation is obtained probably due to shrinking of ECG film which leads to lower surface area; so, the optimum reduction potential and reduction time are -1200 mV and 15 min. respectively. A comparison between the electrochemical activities toward methanol electro-oxidation of different surfaces used in this paper in addition to some other surfaces used in other literatures is illustrated in Table 2. It is clear that our methods give better electrochemical activity as predicted from our highest electro-oxidation peak current.

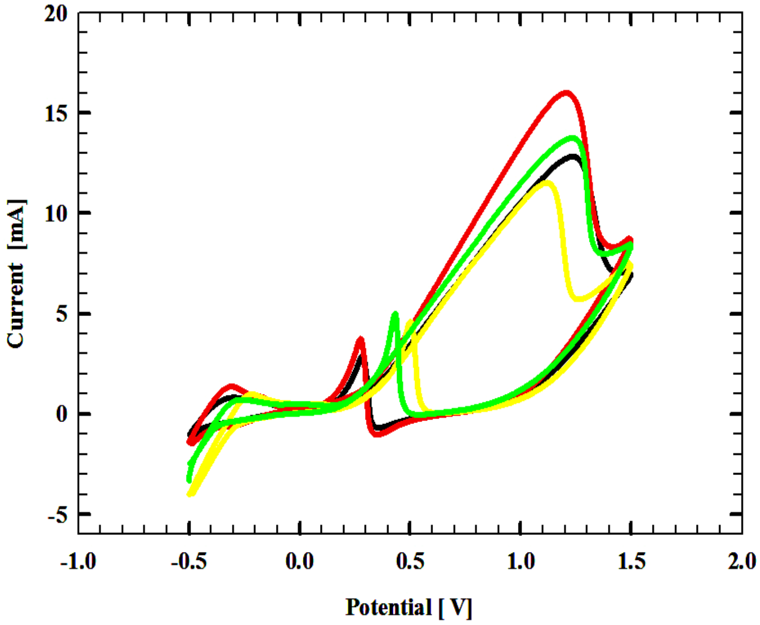
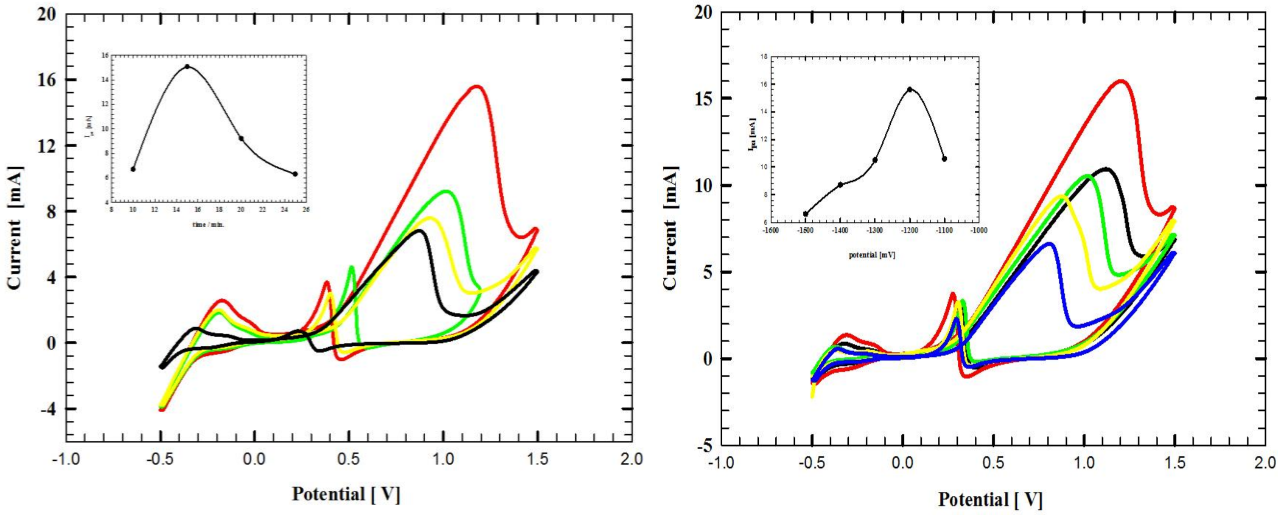


**Figure 10.** Cyclic Voltammetry showing a comparison between CCG and ECG, —GC/CCG/Pt+Pd and —GC/ECG/Pt+Pd, —GC/CCG/Pt+Ru,—GC/ECG/Pt+Ru in 0.5M MeOH+0.1M $H_2SO_4$.



**A** **B**

**Figure 11.** Cyclic voltammetry showing (A) the effect of reduction time of GO for GC/EGC/Pt-Pd in 0.5M $CH_3OH$ +0.1M $H_2SO_4$, — 10 minutes, — 15 minutes, — 20 minutes, —25 minutes and (B) potential of GO for GC/EGC/Pt-Pd in 0.5M $CH_3OH$ +0.1M $H_2SO_4$, — -1100 mV, — -1200 mV, — -1300 mV, —-1400 mV —-1500 mV.

**Table 2**. Comparison of electrocatalytic activity of different electrode surfaces in 0.5M $CH_3OH$ in 0.1M $H_2SO_4$, (Pt-Pd catalyst was deposited over the electrode surfaces by 30 cycles from -250 mV to +650 mV, scan rate 50 mV/s while Pt-Ru was deposited by 15 cycles from -1000 mV to 0.0 V scan rate 50 mV/s). The values of peak current and potential derived from different literatures are included to compare with our electrochemical activity.

| Electrode | $I_{pa}$ | $E_{pa}$[mV] |
|---|---|---|
| GC/Pt-Pd | 7 mA | 966 |
| GC/Pt-Ru | 2.6 mA | 624 |
| GC/CCG/Pt-Pd | 12.8 mA(113 mA/$cm^2$) | 1230 |
| GC/ECG/Pt-Pd | 15.6 mA(138 mA/$cm^2$) | 1200 |
| GC/CCG/Pt-Ru | 13.5 mA(133 mA/$cm^2$) | 1200 |
| GC/ECG/Pt-Ru | 11 mA(108.4 mA/$cm^2$) | 1119 |
| ($G-Pd_1-Pt_3$) Ref. [31] | 394 mA/$mg_{pt}$ (80 mA/$cm^2$) | 650 |
| (graphene/Pt) Ref. [11] | 200 mA/$mg_{pt}$ (45 mA/$cm^2$) | 652 |
| (GNS/Pt-Ru) Ref. [5] | 5.4 mA(0.113 mA.$g_{pt}$/$m^2$) | 700 |
| (graphene/Pt) Ref [15] | 19.1 mA/ $cm^2$ | 650 |
| (ECG/Pt) Ref. [14] | 7.4 mA/ $cm^2$ | 920 |

## 4. CONCLUSIONS

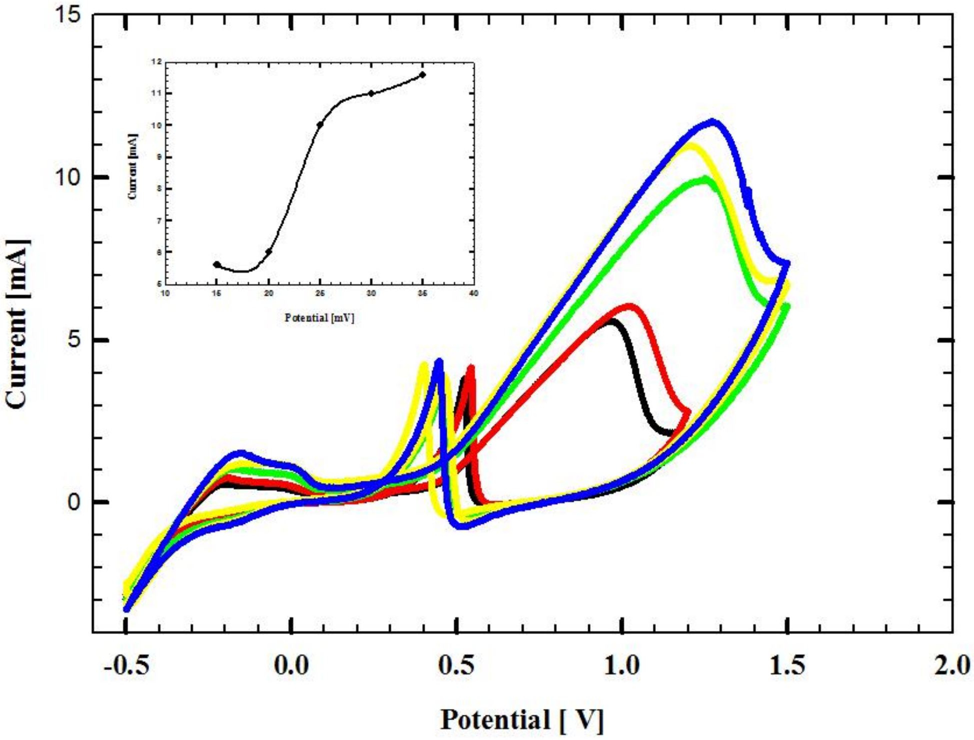
We found that excellent electrocatalytic properties were observed in presence of graphene as a substrate where, the electrochemical activity of the catalysts or co-catalysts toward methanol oxidation increases to two or five times more than in absence of it depending on the type of co-catalysts used, that is probably due to high surface area of graphene which gives higher dispersion of nanoparticles on it. Using different co-catalysts supported on graphene we found that both Pt-Pd and Pt-Ru co-catalysts are good co-catalysts for methanol oxidation but Pt-Ru is more favorable due to its high electrocatalytic behavior even with its lower loading which indicates that Ru has higher ability for removing carbonaceous species hence, it has higher ability in minimizing the poisoning of Pt that is clear from the results of long term stability. Also the Pt-Ru catalyst graphene sub-micron composite prepared by this method gives higher current density 133 mA/$cm^2$ compared to the other methods of preparation mentioned in the literature [5, 11, 14, 15, and 31]. Preparing graphene sheets by two different techniques, chemical method based on microwave and electrochemical method we found that electrochemical method gives comparable electrocatalytic activity toward methanol oxidation with that is prepared via chemical method but the advantage of electrochemically reduced one is the amusing of toxic reductant as hydrazine hydrate.

## ACKNOWLEDGEMENT

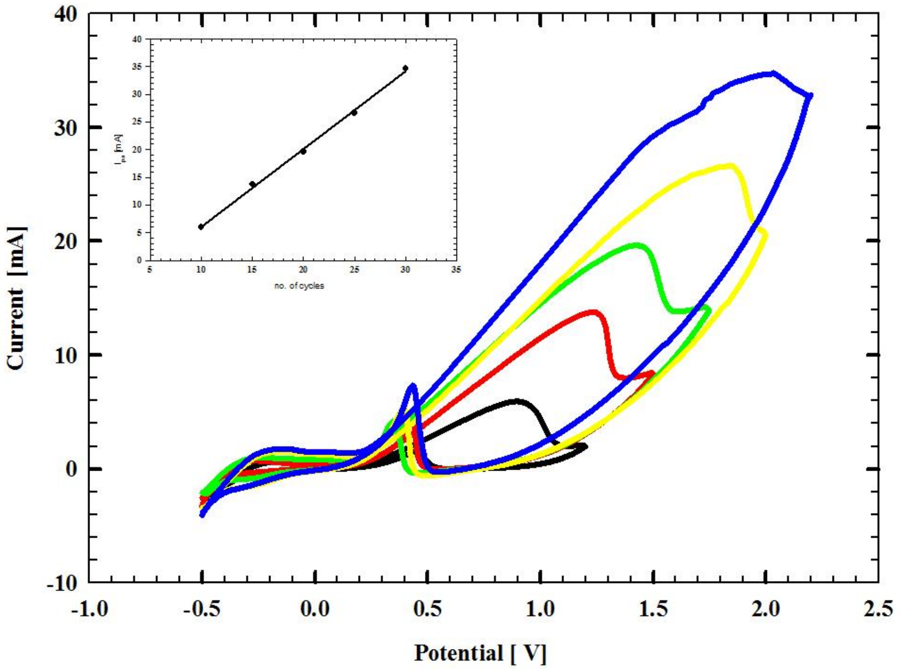
The authors would like to express their gratitude to Cairo University (Office of Vice President for Graduate Studies and Research) for providing partial financial support through "The Young Researchers' Program." We want also to thank the Faculty of Science Central Laboratory Facilities for the use of AFM and SEM.

## References

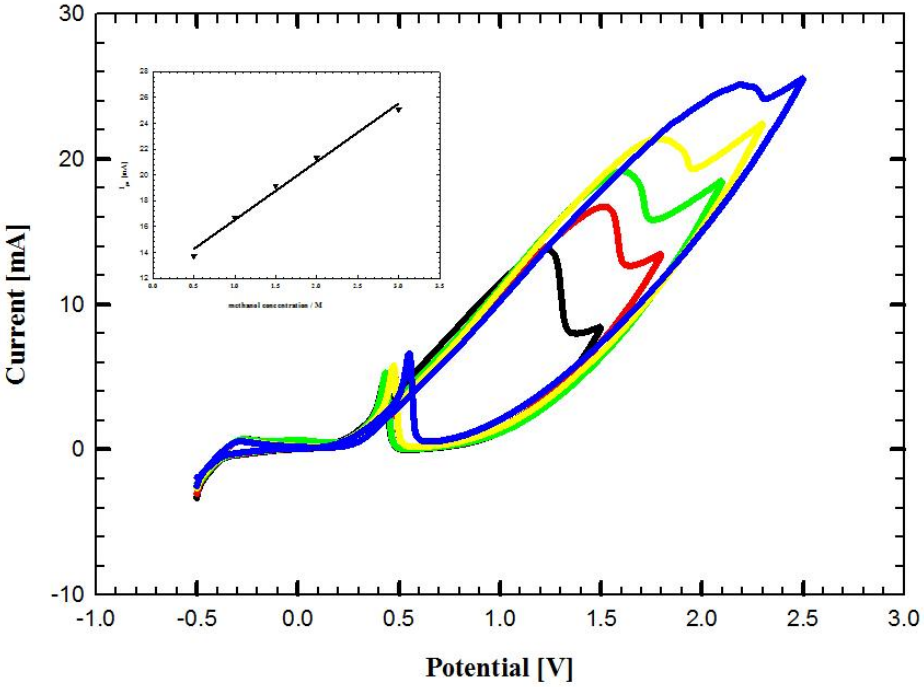
1. P. Serp, M. Corrias and P. Kalck, *App. Catal.: A General* 253 (2003)337.
2. Y. C. Xing, L. Li, C. C. Chusuei and R. V. Hull, *Langmuir* 21(2005) 4185.
3. D. Bom, R. Andrews, D. Jacques, J. Authony, B. L. Chen, M. S. Meieve and J. P. Seleque, *Nano Lett.*, 2 (2002)615.
4. D. A. Stevens, M. T. Hicks, G. M. Haugen, J. R. Dahn, D. A. Stevens, M. T. Hicks, G. M. Haugen and J. R. Dahn, *J. Electrochem., Soc*. 152(2005) A2309.
5. S. Yool Bong, Y. Rae Kim, I. Kim Seunghee Woo, S. Yun Uhm, J. Lee and H. Kim, *Electrochem. Comm.* 11(2010) 129.
6. L. Tang, Y. Wang, Y. Li, H. Feng, J. Lu and J. Li, *Adv. Funct. Mater*., 19 (2009) 2782
7. N. M. R. Peres, *Vacuum*, 83 (2009)1248.
8. O. Leenearts, B. Partoens and F. M. Peeters, *J. Microelectr*., 40 (2009) 860.
9. J. Wintterling and M.-L. Bocquet, *Sur Science*, 603(2009) 1841.
10. C. J. Pool, *Solid State Comm.*, 150 (2010) 632.
11. Y. Li, L. Tang and J. Li, *Electrochem. Comm.*, 11 (2009) 846.
12. J. Wu, Y. Wang, D. Zhang and B. Hou, *J. Power Source*, 196 (2011)1141.
13. M. Zheng, K. Takei, B. Hsia, H. fang, X. Zhang, N. Ferralis, H. Ko, Y.-L. Chueh, Y. Zhang, R. Mabudian and A. Javey, *Appl. Phys. Let.*, 96 (2010) 063110.
14. S. Liu, J. Wang, J. Zeng, J. Ou, Z. Li, X. Liu and S. Yang, *J. Power Sources*, 195 (2010) 4628.
15. L. Dong, R. Reddy, S. Gari, Z. Li, M.M. Craig and S. Hou, *Carbon*, 48 (2010) 781.
16. Z. Peralta-Inga, J.S. Murry, M.E. Grice, S. Boyd, C.J. O'Conner and P. Politzer, *J. Mol. Str. (Theochem.)*, 549 (2001)147.
17. R. T. S. Oliveira, M. C. Santos, B. G. Marcussi, S. T. Tanimoto, L. O. S. Bulh˜oes and E. C. Pereira, *J. Power Sources*, 157 (2006) 212.
18. A. Galal, N. F. Atta, S. A. Darwish, S. M. Ali, *Top Catalysis*, 47 (2008) 73.
19. M. Wang, D.-J. Guo and H.-L. Li, J. *Solid State Chem*., 178 (2005) 1996.
20. Y. Zhao, X. Yang, J. Tian, F. Wang and L. Zhan, Int. *J. Hydrogen Energ.*, 35 (2010) 3249.
21. Y. Lu and R. G. Reddy, Int. *J. Hydrogen Energ.*, 33 (2008) 393.
22. G. Yong-Ping, H. Hui and Z. Wen-Kui, *Trans. Nonferrous Met. SOC China*, 17 (2008) 214.
23. H. Gao, S. Liao, J. Zeng and Y. Xie, *J. Power Sources*, 196 (2011) 54.
24. V. Selvaraj and M. Alagar, Electrochem. Comm., 9 (2007) 1145.
25. W. S. Hummers and R. E. Offeman, *J Am. Chem. Soc.* 80 (1958)1339.
26. H. M. A. Hassan, V. Abdelsayed, A. R. S. Khder, K.M. Abou Zeid, J. Terner, M. S. El-Shall, S.I. Al-Resayes and A.A. El-Azhary, *Mater. Chem.* 19 (2009) 3832.
27. R. B. de Lima, M. P. Massafera, E. A. Batista and T. Iwasita, *J. Electroanal. Chem*., 603 (2007) 142.
28. V. C. Tong, L. M. Chen, M. J. Allen, J. K. Wassail, K. R. Nelson, B. Kaner and Y. Yang, *Nano Lett.* 9 (2009) 1949.
29. H. L. Go, X.F. Wang, Q.Y. Ian, F. B. Wang and X. H. Ixia, *ACS Nano* 3 (2009) 2653.
30. G. K. Rajesh, S. S. Path, *J Phys. Chem.* C, 113 (2009) 7985.



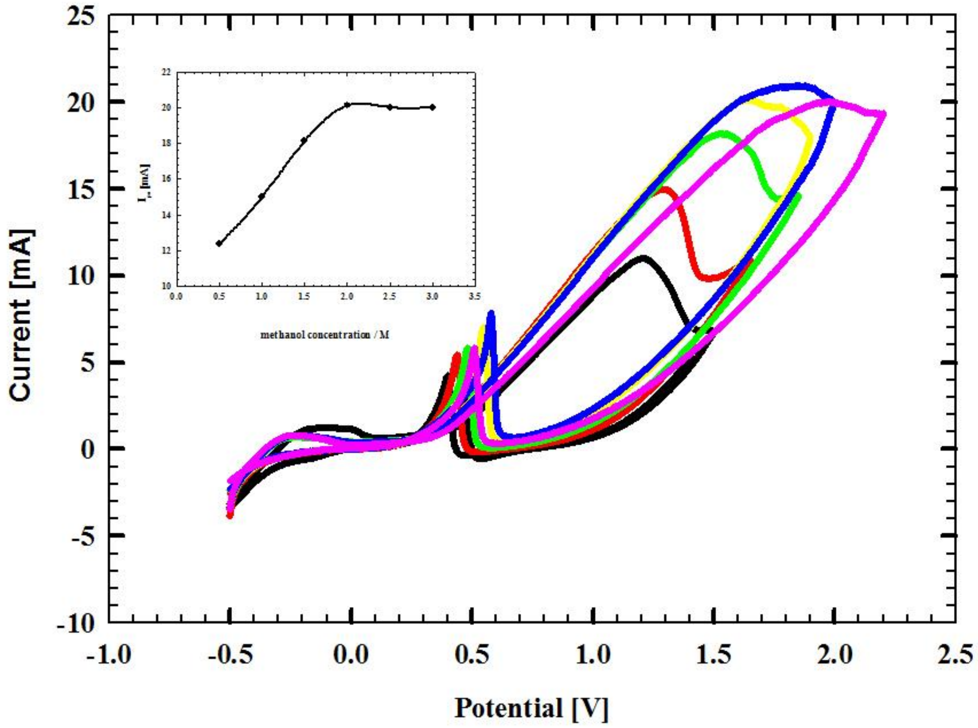
**Supplementary (1)** cyclic voltammetry showing the effect of co-catalyst loading of Pt+Pd (3:1) supported on CCG, — 15, — 20, — 25, —30 and —35 cycles in 0.5M $CH_3OH$ + 0.1M $H_2SO_4$, scan rate 50 mV/s.



**Supplementary (2)** cyclic voltammetry showing the effect of co-catalyst loading of Pt+Ru (3:1) supported on CCG, — 10, — 15, — 20, —25 and —30 cycles in 0.5M $CH_3OH$ + 0.1M $H_2SO_4$, scan rate 50 mV/s.



**Supplementary (3)** Cyclic voltammetry of GC/G/Pt+Pd (3:1) at different concentrations of methanol, — 0.1M, — 0.5M, — 1.0M, —1.5M,—2.0M, scan rate 50 mV/s.



**Supplementary (4)** Cyclic voltammetry of GC/G/Pt+Ru(3:1) at different concentrations of methanol, — 0.5M, — 1.0M, — 1.5M, —2.0M,—3.0M, scan rate 50 mV/s.