



Investigation of the Synergism Effect and Electrocatalytic Activities of Pt and Ru Nanoparticles Supported on the Carbon Aerogel-Carbon Nanotube (CA-CNT) for Methanol Oxidation Reaction (MOR)

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PAPER INFO
Paper history:

Received 14 June 2020

Accepted in revised form 17 August 2020

Keywords:

 Fuel Cell,
Methanol,
Synergism,
Aerogel,
Nanotube

A B S T R A C T

Given that the catalyst and catalyst support properties have a key role to play in the electrochemical activity of fuel cells, in this research, the synergism effect of Pt and Ru nanoparticles reduced on catalyst support [synthesized Carbon Aerogel-Carbon Nanotube (CA-CNT)] was investigated. The catalyst support was synthesized by sol-gel method and the catalyst nanoparticles were reduced on catalyst support using impregnation and hydrothermal method. Different molar ratios of Pt:Ru (i.e., 0:1, 1:0, 3:1, 2:1, 1:1, 1:2, and 1:3) were applied as electrocatalysts for Methanol Oxidation Reaction (MOR). The electrochemical performance of these catalysts was compared with that of commercial Pt/C (20 % wt) for MOR. The physical properties of the synthesized catalyst support (CNT-CA) were studied using FESEM and BET techniques. Moreover, XRD and ICP analyses were employed for investigating each of the synthesized catalyst (Pt/CNT-CA and Ru/CNT-CA). The cyclic voltammetry and chronoamperometry methods were used to conduct electrochemical analysis. Research results indicated that synthesis methods were reliable. Moreover, CNT-CA had a proper performance as the catalyst support and the Pt:Ru with a 3:1 molar ratio was the best catalyst among all the synthesized catalysts for MOR.

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<https://doi.org/10.30501/jree.2020.234091.1116>
1. INTRODUCTION

Recently, fuel cells have been widely considered as a renewable power source. This is a device that produces electrical energy from chemical energy with high efficiency and without pollution. Among all fuel cells, Polymer Exchange Membrane Fuel Cell (PEMFC) and Direct Methanol Fuel Cell (DMFC) have been widespread investigated due to their good commercial abilities. These work at low temperatures. Since DMFCs operate on liquid fuel and do not need complex apparatuses for humidification and heat management, they are considered as a promising choice for energy industrials in the future [1, 2]. However, a significant challenge of commercialization is the intrinsic cost of these fuel cells. Catalyst layer is an important component of the fuel cell because the reactions occur in it. This layer contains catalyst particles and carbon material as catalyst support [3,4]. Considering the specific properties of platinum (Pt) including high catalytic activity, chemical stability, and high exchange current density, it is the best candidate for the catalyst layer. The carbon black Vulcan XC-72 is commonly used as a catalyst support [5].

The main cost of fuel cell is for the catalyst materials. Different approaches have been attempted so far to reduce the cost and enhance the performance of a fuel cell simultaneously. Some approaches can be pointed out that use

multi metal as a catalyst and the improved structure of carbon as a catalyst support. Therefore, the researchers concentrate on use of either Pt alloys or catalyst support materials to reinforce the electrocatalytic efficiency of Pt [6-11].

Bimetallic Pt-Ru electrocatalyst is one of the most widespread ones used due to its bifunctional mechanism for Methanol Oxidation Reaction (MOR) [12-17]. However, the best optimal Pt-Ru ratio has not reached wide agreement. Many studies have found that the 1:1 ratio of Pt: Ru was the best [18-21], but some of researchers reported that the other ratio was optimal for enhancing MOR catalytic activity [22, 23].

In recent years, the role of the nanostructure of carbon supports such as Carbon Nanotubes (CNTs), Carbon Nanofibers (CNFs), carbon aerogels, and nano-plates of graphene has received remarkable interest [24,25]. Some characteristics of carbon nanostructure lead to an efficient MOR, which is the main reason for using them as a catalyst support [26].

It is well known that one of the important factors in the catalytic performance of the electrode in fuel cell is the three-phase zone formation and it is dependent upon the interfacial among the catalyst (solid), electrolyte (liquid), and reactant (gas). Therefore, surface area, pore size, and electrical conductivity of the catalyst support could be very significant in attaining high electrocatalytic activity [11,27,28]. Since the CA has a unique structure and properties such as high porosity, high surface area, and chemical stability, it can be used as a catalyst support to enhance electrocatalytic activities [29- 33]. The CNT showed high electrical conductivity as the

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 URL: http://www.jree.ir/article_112868.html

catalyst support and improved the CA conductivity. For this reason, in many research works, good performances were obtained using the above materials [34,35].

According to the mentioned literatures, two points can be observed: 1) each of CNT or CA has been used as a catalyst support separately; 2) Pt/Ru is synthesized as an alloy on carbon particles. The present research attempts to study the effect of using CNT and CA simultaneously (i.e., CNT-CA) as a catalyst support. Moreover, Pt and Ru are deposited on CNT-CA separately; then, an attempt was made to investigate the electrochemical performance of the mixture of the Pt/CNT-CA and Ru/CNT-CA at different ratios of MOR. In this case, the structure of Pt as an effective and important catalyst is maintained; besides, the presence of Ru has positive effect on the performance of the electrode for MOR.

This study investigates the synergism effect of CNT containing Carbon Aerogel (CA) as the catalyst support and the Pt with Ru bimetallic catalyst for DMFC. The goal of this research is to specify the optimal molar ratio of Pt:Ru in the presence of synergism effect of CNT-CA. In addition to Pt/CNT-CA and Ru/CNT-CA, we select different proportions of Pt:Ru as 1:1, 2:1, 3:1, 1:3, and 1:2 to study the catalyst performance for MOR. However, we compared the synthesis catalyst with commercial Pt/C for MOR. The comparison of obtained electrochemical parameters of Pt/CNT-CA and those of commercial Pt/C shows that CNT-CA is a more efficient catalyst support than the carbon Vulcan XCR72. Our results such as EAS and the ratio of forward to backward peak current (I_f/I_r) indicate that the Pt:Ru with 3:1 ratio has the best performance among all the catalysts studied in this research.

2. EXPERIMENTAL

2.1. Materials

Multi-walled carbon nanotubes were supplied from NeutrinoNeunano. Resorcinol ($C_6H_4(OH)_2$), formaldehyde (HC HO), sodium carbonate (Na_2CO_3), and solvents were supplied from Merck. In addition, $RuCl_3 \cdot 3H_2O$, $H_2PtCl_6 \cdot 6H_2O$, and Nafion solution (5 %) were prepared from Aldrich. Ethylene glycol, glycerol, and 2-propanol were prepared from Merck.

The commercial Pt/C (10 wt % Electrochem Inc.) was used to be compared with the synthesized catalyst.

2.2. Catalyst support (CNT- CA) synthesis

The first step is to functionalize the catalyst support. To this end, the adequate amount of synthesized CNT-CA was refluxed in HNO_3 (MERCK) at 80 °C for 4 h. In the next step, CNT-CA solid phase was separated using centrifugal (ROTINA 46) and rinsed by distilled water.

The powder was then dried at 80 °C for 24 h. Pretreated CNT-CA was divided into 2 parts. One of them was used for Pt/CNT-CA synthesis and the other for Ru/CNT-CA synthesis.

The $RuCl_3 \cdot 3H_2O$ which dissolved in diluted HCl and the $H_2PtCl_6 \cdot 6H_2O$ which dissolved in ethylene glycol were used as precursors.

To synthesize the Ru/CNT-CA, the catalyst support (CNT-CA) should be vigorously dispersed in 2-propanol and water (3:1 V/V); then, the precise amount of Ru precursor was added to the mixture drop wise and was sonicated for 20 min. In the next step, the mixture was located in the oven at 85 °C.

Finally, the powder was sintered at 200 °C in furnace under H_2 atmosphere for 2 h.

To synthesize the Pt/CNT-CA, the adequate amount of Pt precursor and sodium citrate solution in ethylene glycol were added to the homogenous mixture of CNT-CA and 2-propanol and water (3:1 V/V) drop by drop. The pH was adjusted to 10.5 with addition of KOH solution to ethylene glycol. Then, it was transferred into a Teflon autoclave and conditioned at 130 °C for 6 h; in the next step, it was centrifuged, washed, and vacuum dried at 70 °C.

2.3. Catalyst layer preparation

As mentioned previously, in this research, different proportions of Pt:Ru were used as electrocatalyst for MOR. Therefore, the desired amount of synthesized Pt/CNT-CA and Ru/CNT-CA was dispersed in mixture of 2-propanol and water (3:1 V/V) and then, Nafion solution (5 % Aldrich) was added. These mixtures were sonicated for 15 min to obtain homogenous catalyst suspensions. Thus, 7 catalysts were prepared and 7 inks containing Pt/CNT-CA, Ru/CNT-CA, and Pt:Ru (1:1, 1:2, 1:3, 2:1 and 3:1) were prepared. Each of them was put on glassy carbon 5 mm in diameter.

2.4. Physical properties

A scanning electron microscope (Model XL30, Philips co.) and a field emission scanning electron microscope (FESEM model MIRA#TESCAN-XMU) were used for investigating the synthesized catalyst support morphology. To obtain the specific surface area of catalyst support, Barrett-Joyner-Halenda analysis was carried out. Four-point probe was used to determine the CNT-CA electrical resistance.

To obtain XRD pattern, XRD (Philips pw3710 diffractometer with a Cu X-ray source operating at 40 kV and 40 mA) analysis was applied to each of the synthesized catalysts. The amount of reduced Pt and Ru was specified using Inductive Coupled Plasma (ICP) method (ICPOES, Varian Vista-PRO, Australia); for this purpose, 5 mg of each synthesized catalyst was solved in a solution of hydrochloric acid and nitric acid (3/1).

2.5. Electrochemical measurement

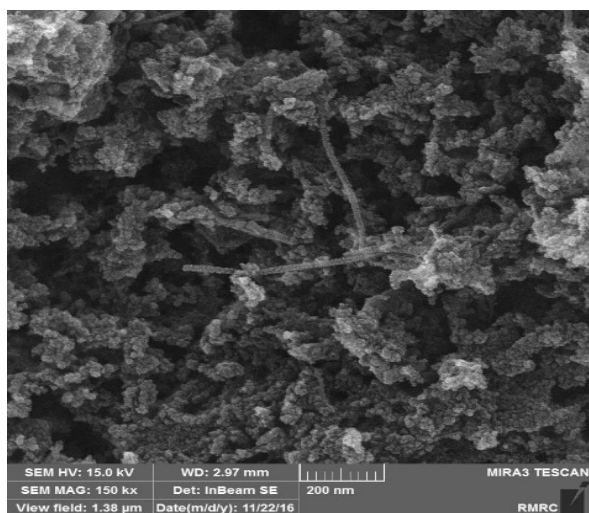
For electrochemical analysis, an EG&G Princeton Applied Research Model 2273 instrument was used to specify the electrochemical properties of the catalyst. All electrochemical measurements were carried out in a conventional three-electrode cell. In this cell, the reference electrode (Ag/AgCl) was located near the working electrode (catalyst on glassy carbon with 5mm in diameter) and the applied counter electrode was Pt-plate. Cyclic Voltammetry (CV) was carried out in two conditions, one of which in 0.5 M H_2SO_4 and the other in 0.5 M H_2SO_4 + 2 M CH_3OH ; for both of them, Ar was flowing. The chronoamperometry was performed in 0.5 M H_2SO_4 + 2 M CH_3OH . All measurements were carried out at 25 °C.

3. RESULTS AND DISCUSSION

3.1. Catalyst support properties

The structure and morphology of the catalyst support was studied by the Field Emission Scanning Electron Microscopy (FESEM).

As shown in Figure 1, the structure of CNT-CA consists of entangled carbon nanotubes surrounded by numerous carbon nanoparticles produced during the pyrolysis process of the organic gel. The dark contrast regions suggest the porous structure. The presence of the pores is further confirmed by BJH analysis. According to the EDS analysis (Fig. 1), the sample was essentially composed of carbon with a small amount of oxygen contained in the surface functional groups. A trace amount of sodium was also detected as impurity.



| Elt | Line | Int | K | Kr | W% | A % | ZAF |
|-----|------|------|--------|--------|-------|-------|--------|
| C | Ka | 936 | 0.9932 | 0.9217 | 96.71 | 97.61 | 0.9516 |
| O | Ka | 7.6 | 0.0040 | 0.0037 | 2.83 | 2.14 | 0.1321 |
| Na | Ka | 13.9 | 0.0028 | 0.0026 | 0.47 | 0.25 | 0.5565 |
| | | | 1 | 0.9280 | 100 | 100 | |

Figure 1. FESEM image of the CNT-C Aerogel, EDS analysis of the CNT-C Aerogel (table).

Nitrogen adsorption/desorption isotherm of the catalyst support at 77 K, which is of IV type, is seen in Figure 2, showing a hysteresis loop of H3 type [37]. This can be due to capillary condensation, indicating the presence of mesopores in the structure. Indeed, BJH analysis showed the existence of both micro and meso pores in the structure with an average pore diameter of 14.97 nm. The measured pore volume was about 1.84 m³/g and the specific surface area obtained by BET model was 491.7 m²/g. Density of the sample was measured by a pycnometer to be around 0.2 g/m³. The chemical inertness and the porous structure with a high surface area fulfill the requirements for the catalyst support. Electrical resistance of the catalyst support was measured by the four-point probe method to be about 14.4x10⁻⁵ ohm.m.

3.2. Catalyst characterization

The XRD patterns of Pt/CNT_CA and Ru/CNT-CA are shown in Figures 3-a and 3-b. In both spectra, the peak centered at about 30° can be ascribed to the CNT_CA.

In Figure 3-a, the peaks at 2θ = 40°, 47°, 68°, and 81° are associated with Pt plates (111), (200), (220), and (311), respectively. This result emphasizes that Pt has successfully been reduced on CNT-CA and the broad peaks indicate that the Pt particles are nanosized.

Figure 3-b shows the peaks at 2θ = 44° that emerged from Ru (100) plate. Therefore, Ru particles were successfully reduced and the broad peaks were due to Ru nano-scaled particles.

According to ICP results, the reduced Pt and Ru were 20 % wt and 16 % wt, respectively. Therefore, synthesis method in this research was applied to reducing Pt and Ru on CNT-CA. It needs to be mentioned that since Ru wt% is lower than Pt wt %, the peak observed in the XRD pattern of Ru is less intense than that of Pt.

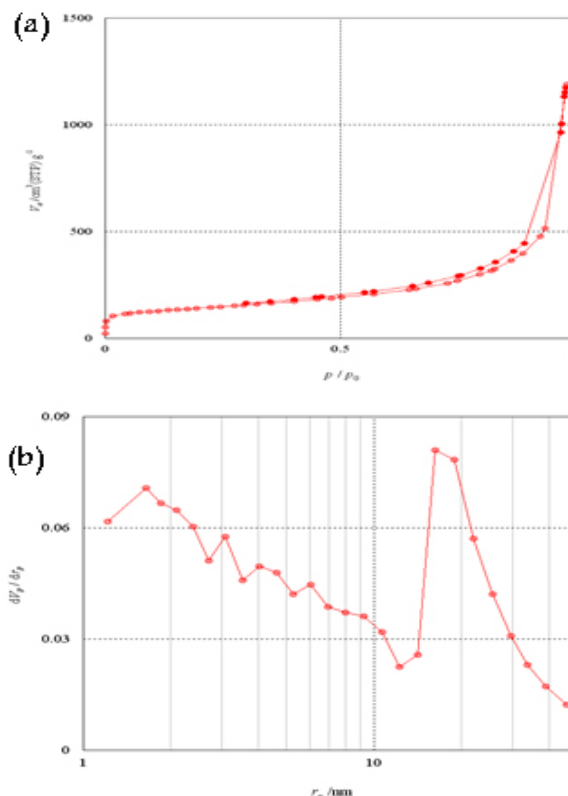


Figure 2. N₂ adsorption/desorption isotherm of the CNT-C/Aerogel (a), BJH plot of pore distribution (b).

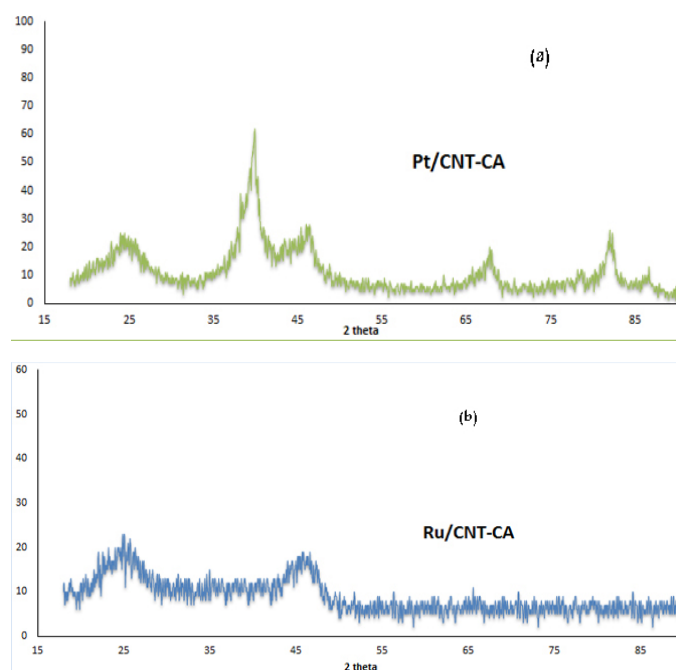


Figure 3. XRD patterns of (a) Pt/CNT-CA and (b) Ru/CNT-CA.

3.3. Electrochemical performance of the catalyst

Cyclic Voltammetry (CV) analysis can be used to calculate the electroactive surface area (EAS). Figure 4 shows the CV

curve of 7 synthesized catalysts and Pt/C in 0.5 M H₂SO₄ solution. The presence of the hydrogen absorption/desorption peaks in CV curves indicates the catalytic activity of the catalysts. The coulombic charge for hydrogen desorption was used to measure the EAS of each catalyst (Table 1) [38]. From the EAS results, it can be concluded that the Pt/ CNT-CA was more active than the commercial Pt/C. This result can be

attributed to catalyst support impact. The CNT-CA can enhance the hydrogen desorption on Pt. On the other hand, the simultaneous presence of Ru/CNT-CA and Pt/CNT-CA in the catalyst reinforced the catalytic activity for hydrogen desorption. In Table 1, the catalyst with Pt:Ru of 3:1 ratio has the maximum EAS.

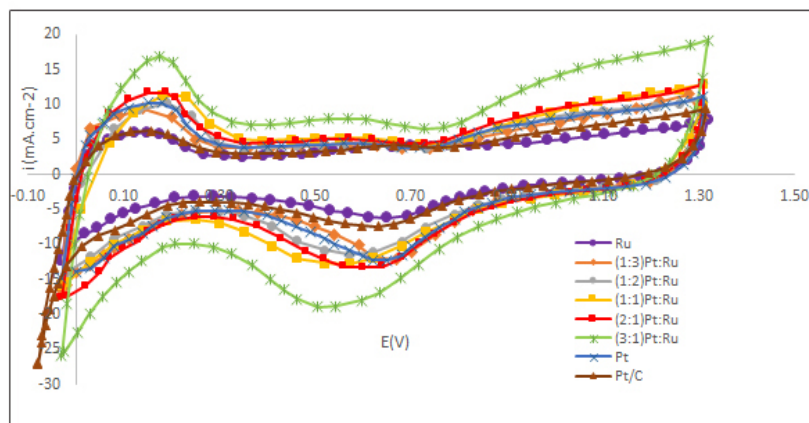


Figure 4. Cyclic voltammetry of synthesized catalysts in 0.5 M H₂SO₄, argon atmosphere, 50 mV.s⁻¹ scan rate at 25 °C.

Moreover, CV analysis in 0.5 M H₂SO₄ + 2 M CH₃OH solution was used to investigate the electrocatalytic activation for MOR (Fig. 5). The shape of curves is similar. In Figure 5, the forward peaks are located between 0.8 and 0.9 V and the backward peaks are visible between 0.4 and 0.6 V. The forward peak (*I_f*) is typically attributed to the MOR and the backward peak (*I_b*) is related to the oxidation of residual intermediate. Note that the current density is related to the reaction rate and the results show that the Pt/ CNT-CA has better behavior than the commercial Pt/C; therefore, the CNT-CA catalyst support could enhance the catalyst performance for MOR. Furthermore, these results emphasize that the Ru

particle presence in catalyst has positive effect for MOR kinetic. Comparison of the obtained results (Table 1) reveals that the catalyst with Pt:Ru ratio of 3:1 has the maximum current density among all the catalysts.

One of the important parameters for evaluating the catalyst performance for MOR is the ratio of forward to backward peak current (*I_f/I_b*). This parameter can be ascribed to the catalyst tolerance so that the higher ratio demonstrates more impressive elimination of the poisoning species on the catalyst surface. Since the catalyst with Pt:Ru ratio of 3:1 has the maximum *I_b/I_f* ratio, it can be concluded that this is the best catalyst for MOR among all the synthesized catalysts.

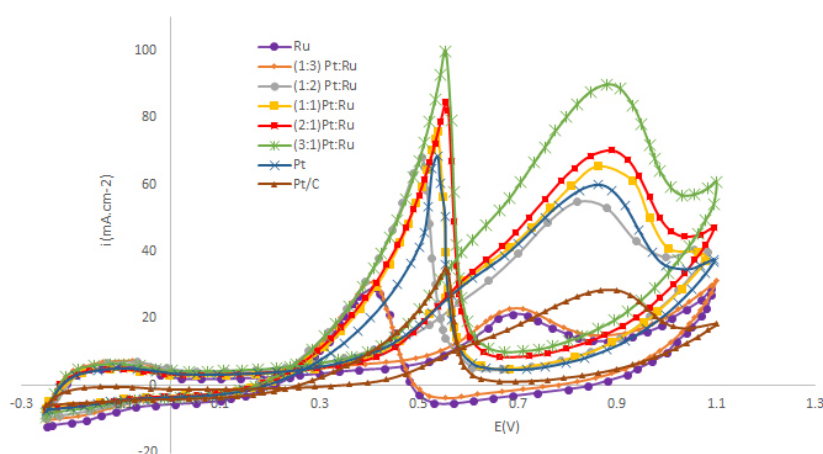


Figure 5. Cyclic voltammetry of synthesized catalysts in 0.5 M H₂SO₄+2 M CH₃OH argon atmosphere, 50 mV.s⁻¹ scan rate at 25 °C.

Table 1. Electrochemical parameter of synthesized catalyst and commercial catalyst.

| Catalyst | EAS (m ² /gr) | <i>i_f</i> (mA.mg _{cat} ⁻¹) | <i>i_b</i> (mA.mg _{cat} ⁻¹) | <i>i_f</i> (mA.cm ⁻²) | <i>i_b</i> (mA.cm ⁻²) | (<i>i_f/i_b</i>) |
|-------------|--------------------------|--|--|---|---|--|
| Ru | 13.3 | 53.5 | 73.25 | 21.4 | 29.3 | 0.73 |
| (1:3) Pt:Ru | 19.71 | 57.52 | 78 | 23.01 | 31.2 | 0.74 |
| (1:2) Pt:Ru | 20.57 | 138.8 | 170.25 | 55.52 | 68.1 | 0.81 |
| (1:1) Pt:Ru | 25.52 | 165.75 | 189.17 | 66.30 | 75.67 | 0.87 |
| (2:1) Pt:Ru | 27.3 | 175.9 | 211.175 | 70.36 | 84.47 | 0.83 |
| (3:1) Pt:Ru | 35.9 | 225.15 | 279.17 | 90.29 | 99.58 | 0.91 |
| Pt | 23.9 | 149.85 | 170.92 | 59.94 | 68.37 | 0.87 |
| Pt/C | 18.7 | 71.47 | 87.35 | 28.59 | 34.94 | 0.81 |

Figure 6 shows the chronoamperometry study of the synthesized catalysts. Comparison of the Pt/CNT-CA and commercial Pt/C results (Fig. 6) reveals that the CNT-CA as a catalyst support has a better performance than Vulcan, as expected. Moreover, the results illustrate that the Pt:Ru with 3:1 ratio performs more properly than the other catalyst. The presence of Ru/CNT-CA in catalyst is not only stabilizing the catalyst particle but also enhancing the MOR current.

The obtained results of this research corroborate that the CNT-CA can modify the catalyst performance for MOR. This

effect can be ascribed to the high surface area, high electron conductivity, and high porosity of the synthesized CNT-CA. Ru catalyst plays an important role in resisting the CO poisoning of the catalyst during the MOR. This results in the active sites of catalyst to be available for MOR.

Since the Pt particles can readily be poisoned by absorbed CO species, Ru presence helps remove the CO poisoning. In fact, this research used the synergistic effect of Ru and found that the Pt:Ru with 3:1 ratio as a catalyst had the greatest effect on MOR.

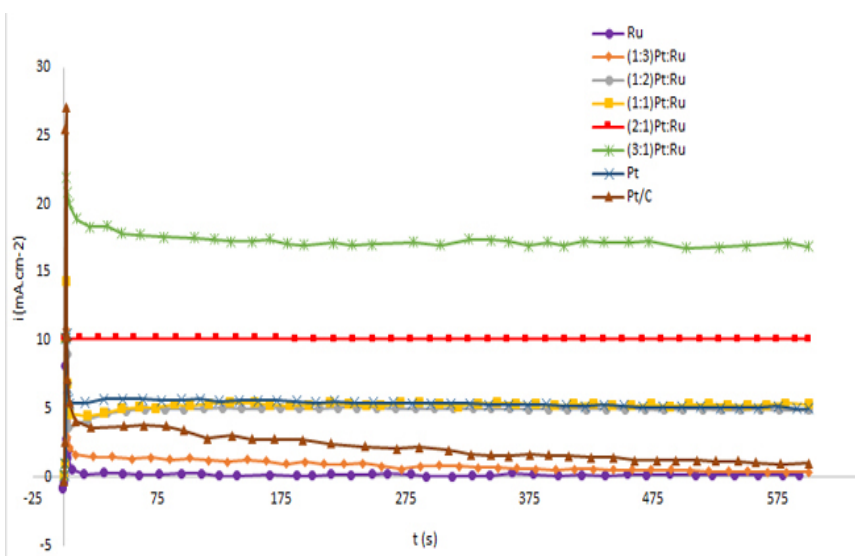


Figure 6. chronoamperometry of synthesized catalyst in 0.5 M H₂SO₄ + 2 M CH₃OH at 0.6 V and 25°C.

4. CONCLUSIONS

In summary, the aim of this research was to investigate not only the effect of simultaneous use of CNT and CA (i.e., CNT-CA) as a catalyst support but also the influence of Ru presence with Pt on the catalyst layer for the MOR reaction. The CNT-CA catalyst support with a high surface area and high electrical conductivity was synthesized by sol-gel method. The catalyst support was distinguished by using SEM, XRD, BET, and four-point probe techniques. Moreover, the catalysts Pt/CNT-CA and Ru/CNT-CA were synthesized by impregnation and hydrothermal methods. Synthesized catalysts were characterized by XRD and ICP technique and the electrochemical activities of the catalysts were studied. Furthermore, the catalysts with different Pt:Ru ratios (1:0,1:1, 2:1, 3:1, 1:2, 1:3 and 0:1) were studied and their performance was compared with the commercial Pt/C. Research results illustrated that: 1) the synthesis methods were reliable, 2) the CNT-CA showed proper performance as the catalyst support, and 3) the Pt:RU with 3:1 molar ratio was the best catalyst for MOR among all the synthesized catalysts.

It is hoped that in future studies, based on the obtained results in this work which indicated an improvement in the performance of the synthesized catalyst compared to the commercial Pt/C for MOR, the effect of Pt/Ru alloy as well as core-shell structure of these two metals deposited on CNT-CA should be considered. The synthesized catalyst will be used as anode of monocell and studied.

5. ACKNOWLEDGEMENT

This work was supported by Materials and Energy Research Center (MERC).

NOMENCLATURE

| | |
|-------|-----------------------------|
| EAS | Electro active surface area |
| CNT | Carbon nanotube |
| CA | Carbon aerogel |
| i_f | Forward peak current |
| i_b | Backwarded peak current |

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