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Electrochemical performance improvement of the catalyst of the methanol micro-fuel cell using carbon nanotubes

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ABSTRACT

Due to low working temperature, high energy density and low pollution, proton exchange fuel cells have been investigated under different operating conditions in different applications. Using platinum catalyst in methanol fuel cell leads to increasing the cost of this kind of fuel cells which is considered as a barrier to commercialism of this technology. For this reason, a lot of efforts have been made to reduce the loading of the catalyst required on different supports. In this study, carbon black (CB) and carbon nanotubes (CNT) have been used as catalyst supports of the fuel cell as well as using the double-metal combination of platinum-ruthenium (PtRu) as anode electrode catalyst and platinum (Pt) as cathode electrode catalyst. The performance of these two types of the electro-catalyst in oxidation reaction of methanol has been compared based on electrochemical tests. Results showed that the carbon nanotubes increase the performance of the micro-fuel cell by 37% at maximum power density, compared to the carbon black. Based on thee-electrode tests of chronoamperometry and voltammetry, it was found that oxidation onset potential of methanol for CNT has been around 20% less than CB, leading to the kinetic improvement of the oxidation reaction. In addition, the active electrochemical surface area of catalyst has been increased up to 90% by using CNT compared to CB which shows the significant rise of the electrocatalytic activity in CNT supported catalyst with 62% increase in current density of methanol oxidation reaction respect to CB supported one. Moreover, the resistance of CNT supported sample to poisonous intermediate species has been found 3% more than CB supported one. According to the chronoamperometry test results, it was concluded that the performance and sustainability of NCT electro-catalyst shows remarkable improvement compared to CB electro-catalyst in long term.

Keywords: fuel cell; carbon nanotube; catalyst; platinum-ruthenium

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1-Introduction

The fuel cell converts chemical energy directly into heat and power from a chemical reaction mainly between oxygen and hydrogen, without combustion. A fuel cell is composed of an electrolyte membrane combined with fuel electrode and oxidizing electrode [1]. High efficiency, environmental compatibility, simple maintenance, different working fuel, low noise pollution, different application, simultaneous production of heat and power are some of the benefits of the fuel cells [2]. Due to its low working temperature, high energy density and low emission, the performance of the proton exchange fuel cell have been studied by many researchers in transportation industry [3]. The membrane is the core of fuel cell which is generally made by heat pressing of the penetration layers, catalytic layer and micro porous layer on both sides of the membrane. The electricity is generated from the complex chemical and physical process occurs at sides of the membrane. Although using precious metals like platinum and platinum-based alloys, as reaction catalyst, is expensive but they lead to more sustainability in the fuel cell performance. Generally, uniform distribution of the platinum-based catalysts across the common electrodes increases the cost. Furthermore, non-uniform distribution of the current density by membrane decreases the lifetime of membrane, catalyst and carbon [4]. Methanol fuel cell has a high potential for using in electronic products. Methanol, as a fuel, has high energy density and can be obtained and used constantly from different natural gas, coal and bio mass resources.

Even though many researches have been conducted on methanol fuel cells during recent two decades but there are still challenges that should be addressed. One of these challenges is to use a cost-effective catalyst [5]. Electro-catalyzation of the oxygen reaction is a crucial step in fuel cells utilization [6]. Integration of Platinum (Pt) and other metals with different stoichiometric ratios foe CNT support affects the active electrochemical area in catalytic oxidation reactions [7]. For any decades, finding anode catalyst for fuel cells with high activity and stability has been a great challenge [8]. Platinum-ruthenium (PtRu) catalyst usually is used as anode catalyst in direct methanol fuel cells [9]. Due to high cost of catalyst and preventing from overusing it, catalytic supports with high specific surface area should be used. Carbon uses as the electro-catalyst support more than the oxide of other metals because of its high specific surface area, high resistance to acid and easy recovery compared to metal catalysts. Carbon black is also used as catalyst support of many metals but corrosion is one of its problems when the catalyst nanoparticles trap inside it.

By comparing the performance of PtAu/C and PtRu/C, Xu et al [10] concluded that PtAu/C has more activity for MOR and longer durability than PtRu/C. Stability of AU is more than RU. Thiagarajan et al [11] used Pt-Ru-NiTiO3 nanoparticles, with particle size of 2.9 nm, as catalyst on carbon and observed its uniform distribution on carbon. They found that it has higher catalytic activity than PtRu/C and the onset potential became 60mV more negative. Sui et al. [12], by using PtRu/C-TiN instead of PtRu/C and increasing its stability, increased the electro-catalyst activity and its durability after 1000 cycle up to 47.3% and 6.5%, respectively. By studying numerically the effect of CO emission on performance of the PEM fuel cell using PtRu/C and Pt/C catalysts, Bilondi et al. [13] resulted that with increasing the cell temperature and using PtRu/C instead of Pt/C (at low temperatures), the performance of the fuel cell is improved while using PtRu/C at high temperatures leads to minor improvement of fuel cell. Xu et al. [9] coated PtRu nanoparticles with cerium oxide (CeO_2) which increased the oxidation reaction activity of methanol by 2.8 compared to bare PtRu electrocatalyst and the CO oxidation peaks shift by 60 mV negatively respect to PtRu and also the power density increased 1% per each cm^2. Sun et al [14] improved the performance of the catalyst of the fuel cell with using PtRu@h-BN/C instead of PtRu/C. Altarawneh et al [15] used PtNi as catalyst which its performance was similar to Pt/C at low potential while it was significantly better for complete oxidation of methanol and caused to performance improvement of the fuel cell. Dhelipan et al [16] examined the performance of the activated fuel cell which carbon black was used as its electrode. They used an electrode with area of 0.071 cm^2, platinum as catalyst and activated carbon as catalyst support. The micro-fuel cell was tested in temperature of 60 °C where platinum on carbon was used as cathode catalyst and commercial catalyst was used as anode. They compared the cost of using 10% platinum on Vulcan with carbon black and their results showed that output voltage was 0.2 to 1 V, current density for activated carbon was 1mA/cm^2 and current density for Vulcan carbon was 5.84 mA/cm^2. The tests were conducted in 0.1 M sulfuric acid solution and the maximum generated power was 19 mV/ cm^2. Since the benefit of using activated carbon as catalyst support is its high surface area, Yang et al [17] used Immobilized material on active carbon at minimum material consumption. The tests were accomplished to measure the power generation mostly with iron and a low amount of nitrogen to minimize the cost. In addition, the performance of the Fe–N–C on AC catalyst was compared with Fe–N and cathodes made with the platinum catalyst. Fe–N–C catalyst led to more power generation compared to the other catalysts. The maximum power was reported 4.7 W/m^2 when the concentration of solution was increased. The other cathodes they made were Co–N–C/AC and Na–N–C/AC and the generated power was even more when platinum was used as catalyst. The best amount of power generation was 2.6 W/m^2 or 0.26 mW/cm^2 for Fe–N–C/AC as cathode and the highest ampere and voltage were 0.25 mA and 0.8 V respectively. A new catalyst with blending activated carbon on cathode electrode and using graphene oxide on nickel as anode was tested by Yang et al [18] and compared with the cathodes that only activated carbon was used in them. The highest power density was reported 0.225 mW/cm^2 and the mazimum current density was 1.3 mA/cm^2.

Ahmed et al. [19] used Co_3O_4 on CNT, which has more stability and activity than Pt/C, in fuel cells in order to increase the activity and decrease the cost. Liu et al [20] doping Carbon nanotubes with nitrogen which led to better performance compared to pure CNT.

Other researchers made CeO_2 and xH_2O nanoparticles with OH groups using solvothermal method and blend it with Pt/CNT via ultrasonic. Chronoamperometry test showed that the current density for CeO2·xH2O/Pt/CNT is around 57 times larger than Pt/CNT which was finally suggested to use modified CeO_2xH_2O nanoparticles on Pt/CNT or PtRu/C [8]. By comparing MWCNT/Pt, DWCNT/Pt and SWCNT/Pt, Dongmulati et al. [21] concluded that using MWCNT/Pt as catalyst in fuel cells is better than two other one due to its high specific surface area. Because of their low cost and high stability, Liu et al. [6] used non-metal catalysts instead of Pt/C which led to better results. Eckardt et al. [22] investigated the stability and activity of platinum nanoparticles on titania-CN and some other materials as catalyst support which the physical and electrochemical properties as well as stability of this catalyst was reported better than commercial Pt/C, Pt/TiO2 and Pt/CNT. Ghasem et al [23] used nickel and Palladium nanoparticles on MWCNT which results showed that Ni@Pd/MWCNT catalysts have good catalytic activity respect to methanol oxidation in alkaline solutions and Ni@Pd/MWCNT can be used as a low-cost and suitable catalyst for DMFC. Bharti et al. [24] studied the he role of two types of surfactants on the synthesis and properties of MWCNT and compared it with the no-surfactant condition. When sodium dodecyl sulfate was used as surfactant, more catalytic activity and better results was reported compared to Pt-Pd/CNT. Themsirimongkon et al. [7] covered carbon nanotubes with different metallic compositions, such as Pd and Au, in order to improve the electrocatalytic activity of alcohol oxidation. They observed uniform distribution of the metal particles with diameters of 2 to 6 nm in their experiments. Due to more active electrochemical surface area and lower onset potential, low charge transfer resistance and high peak current densities, the alcohol oxidation kinetic for tested catalysts was reported better than commercial PtRu/CNT. Panrod et al. [25] evaluated the effect of mono- and bimetallic compositions on manganese dioxide and modified carbon nanotubes in order to increase the alcohol oxidation. CNT/MnO2/1M3Pt (M 1/4 Pd or Au) catalysts showed better activity improvement compared to the other prepared catalysts. By Plasma synthesis of Pt nanoparticles on graphene oxide-carbon nanotubes (Pt/GNTs) and comparing its performance with other prepared nanocomposites and commercial Pt/C, Ma et al. [26] found that Pt/GNT has higher current density and better electrochemical performance. Zhu et al. [27] examined the effect of using platinum on PDDA and CNT as a substitute for Pt/C and Pt/CNT catalysts. Their results showed that Pt/PDDA-CNT has good thermal stability, electrochemical stability and electrocatalytic activity and also leads to platinum consumption reduction. Chen et al. [28] used PteCoN/TiNeCNT as the electrocatalyst of fuel cell and reported better electrochemical performance, higher onset potential and more electron transfer compared to pure platinum. Considering that platinum with carbon black support has low stability and high loss but has good catalytic activity, Cha et al. [29] tested the platinum on carbon black and carbon nanotubes. They used platinum as catalyst both for cathode and anode and reported the maximum currency and voltage of 650 mA and 1 V for carbon black, respectively. Results of using this material in nanotubes showed an increase of 30% in power generation. Abha Bharti et al [30] used different nanotube supports with platinum as catalyst for performance of the fuel cell. They tested platinum on carbon black, monolayer and multi-walled carbon nanotube and graphene. Their results showed that the multi-walled layer carbon nanotube is the best support for platinum. The amount of power for multi-walled layer carbon nanotube was 0.005% more than carbon black, per each gram of platinum. Novika et al. [31] used platinum catalysts on carbon nanotubes and carbon black. Their performance was compared and the maximum power density was achieved for nanotubes. Litkohi et al. [32] used Pt-Ni-Fe composition on carbon nanotube as fuel cell catalyst which led to a more appropriate structure. Despite using less platinum catalyst in comparison to Pt/C, they also found that the power density has increased and the charge transfer resistance has decreased due to using the platinum, nickel and iron composition as catalyst. The increase in power density was 4 times more than that of Pt/C. Zhang et al [33] used platinum as catalyst and carbon nanotube and carbon Vulcan as catalyst supports. Comparing the results showed that the high specific surface area and good electrical conductivity of nanotubes led to better dispersing, decreasing the platinum catalyst consumption and increasing the charge transfer capacity. It was also shown that the current density, diameter and surface area changed by 3.5 fold, 0.6 fold and 2.2 fold per each gram of platinum, respectively. Kaewsai et al. [34] used platinum and cobalt composition on multi-walled carbon nanotube which increased the electrical conductivity, crystallite size and average particle size of the electrochemical surface area leading to high stability of the catalyst.

2. Materials and methods

In order to prepare the electro-catalyst for methanol oxidation reaction, at first, carbon black based catalysts and synthesized carbon nanotubes and then catalyst ink were made.

2.1. Electrocatalyst synthesis

Carbon black, multi-walled nanotubes, hexachloroplatinic acid (H2PtCl6.6H2O), ruthenium chloride (RuCl.3H2O), 2-propanol, sodium borohydride (NaBH4), sodium hydroxide (NaOH), acetone and deionized water were used to synthesis and prepare the catalyst samples. Impregnation reduction method one of the most used methods for electro-catalyst synthesis in which the platinum precursor (for example H2PtCl6 or any other metal as catalyst) is mixed with the material used for support to absorb the platinum precursor on support. Then, the reduction process of the platinum precursor is conducted at liquid or gas phase using a reducing agent such as sodium borohydride, ascorbic acid, ethylene glycol or hydrogen gas. This method can be performed under normal condition and controlled easily by setting the temperature and time of the reaction and type of the solvent and reducing agent which made this method suitable for mass production of the electro-catalysts. In this study, impregnation reduction method has been employed for synthesis of electro-catalyst PtRu with 1:1 atomic ratio using sodium borohydride as reducing agent and isopropanol solvent. At first, 1 gram of Merck (H2PtCl6.6H2O) is solved in 25 mL of deionized water to form a solution of platinum and deionized water with molar concentration of 0.77 mmole/mL and mass concentration of 15.067 mg/mL. But Sigma-Aldrich (RuCl3.XH2O) is used for ruthenium. In order to avoid hydrolyzing the RuCl3 composition during time, 1 gram of Sigma-Aldrich was solved in 25 mL of 0.1 M HCl solution to form a solution of ruthenium with molar concentration of 0.176 mmole/mL and mass concentration of 17.8 mg/mL.

In order to begin the process, 100 mg of CB MWCNT is dispersed homogeneously and uniformly in 100 mL of solvent consisting of isopropyl alcohol (IPA) and deionized water with ratio of 1:2 in the ultrasonic probe device for 1 hour. After that, the required amount of platinum and ruthenium solution (20% of PtRu catalyst by weight) is added to the suspension and is put on the stirrer at ambient temperature for 1 hour. In the next step, the PH of the solution is set to 10% using 0.5 molar of NaOH solution and is put on the stirrer and its temperature is increased up to 60 °C. Then, the required amount of solution of 0.1 molar NABH4 in deionized water is prepared as reducing agent and is added to the suspension drop by drop in the magnetic mixer at 60 °C for 2 to 3 hours. The required sodium borohydride solution for completing the reduction process of metal ions is Pt:NaBH4 with molar ratio of 1:10 and Ru:NaBH4 with ratio of 1:7. After adding the reducing agent, the solution is kept at 60 °C for 2 hours and then is put on the stirrer at ambient temperature for 12 hours to complete the reaction. At the end of this step, electro-catalyst has been synthesized and 4500 rpm centrifuge is used to separate it from ionic pollutants and non-reactive materials. The electro-catalyst is washed with acetone and then with deionized water several times and is put into convection oven at 60 °C to remove the extra water. Finally, the sample is dried at 60 °C for 12 hours.

The goal of electrochemical experiments is to gain important information about the performance of the catalyst and some of its properties in MOR reaction. Voltammetry is a test used for evaluating the performance of the electro-catalyst. In this analysis, the studied materials are put in a semi-cell to measure the performance of them and current intensity is achieved as a function of voltage. The obtained curves are called voltammogram graphs. In these tests, potential is changed at a fixed rate and the intensity of the currents is recorded. In voltammetry tests conducted for measuring the electrocatalytic properties of the catalyst of the methanol oxidation reaction, electrodes with different structure and material are used. Glassy carbon (GC which is more common) electrode or carbon paper (GDE) electrode, with high electric conductivity and given surface area, are used as the working electrode for coating catalyst layer. The counter electrode is usually made of platinum or glassy carbon and is used in the form of bar, wire or plate. The reference electrode can be very divers but the most common types of them are half-cell of saturated calomel and half-cell of Ag/AgCl. All three electrodes are connected to a potentiostat or galvanostat device. It should be noted that in different tests the supporting electrolyte is the half molar solution of H2SO4 and the tests should be conducted under no oxygen condition. For this reason, the electrolyte-electrode set is exposed to a noble gas, such as nitrogen or argon, to remove the oxygen from the environment.

In voltammetry tests, the glassy carbon electrode with diameter of 2 mm, the platinum plate electrode and half-cell of Ag/AgCl were used as working electrode, counter electrode and reference electrode, respectively. In current study, three-electrode voltammetry tests were used for measuring and gaining the cyclic voltammetry graphs in 0.5 M H2SO4 and 1 M CH3OH electrolytes and chronoamperometry test. The NANO RNF potentiostat was used for obtaining the voltammetry graphs. The tests will be discussed separately in next sections.

2.2. Cyclic voltammetry

2.2.1. Chronoamperometry

One of the most important features of the catalyst in the methanol fuel cell is high durability and the ability to maintain the performance in long term. A lot of efforts are put in improving the durability of the catalyst layer. Chronoamperometry test is used to measure this important feature. In this test, the electrodes are put into methanol and acid sulfuric solution, as electrolyte, and nitrogen gas is used to remove the oxygen from the environment. Then a constant voltage, around the peak voltage obtained in CV test, is applied on electrodes and the passing current is recorded. Finally, the graph of variations of the current intensity is plotted in terms of the time. Due to the formation of the carbon monoxide in methanol oxidation reaction, poisoning of part of the catalyst and blocking catalyst pores, the current drops dramatically at first. But after a while, it should reach to a constant and stable current. The more stable the current is, the better electrocatalytic performance and durability the sample has. During fabrication process, catalyst samples synthesized on carbon support is dried in vacuum oven and collected as powder. In order to support the catalyst layer on glassy carbon electrode, at first, it is necessary to prepare catalyst ink and then it should be coating and dried on the electrode to be used for electrochemical tests. Firstly, 1 mg of PtRu/C electro-catalyst is weighted and is dispersed in a solution of carbon:deionized water:isopropanol with ratio of 1:40:200. Therefore, 40 µL of deionized water and 260 µL of isopropanol are added to the sample. 20 µL of 5% nafion solution is added as ionomer to the sample which facilitates exchange of the ions produced from oxidation reaction and keeps catalyst layer on the electrode in electrolyte. After mixing the different components, to make a uniform ink from electro-catalyst, the sample is put into an ultrasonic bath for 30 min so that the catalyst particles are dispersed completely. Meanwhile, the surface of glassy carbon electrode is cleaned by rubbing on damp cloth containing alumina powder and then is cleaned and dried. After this step, 10 µL of catalyst ink is coating under infrared light to dry the ink quickly.

The amount of loaded PtRu on electrode surface area is calculated as follow:

$$\frac{\mathbf{1mg\ cat - supp \times 0.2\ \frac{cat}{cat - supp} \times 10\mu l\ sol}}{\mathbf{(40 + 260 + 20)\ \mu l\ sol}} = \mathbf{6.25 \times 10^{-3} mg\ PtRu}$$

The surface are of the electrode is:

$$\frac{\boldsymbol{\pi}(\mathbf{0.2})^{2}}{\mathbf{4}} = \mathbf{3.14 \times 10^{-2}}\boldsymbol{cm^{2}}$$

As a result, the amount of PtRu loading per surface area is calculated as:

$$\frac{\mathbf{6.25 \times 10^{-3} mg\ PtRu}}{\mathbf{3.14 \times 10^{-2}}\boldsymbol{cm^{2}}} \approx \mathbf{0.2}\ \frac{\mathbf{mg\ PtRu}}{\boldsymbol{cm^{2}}}$$

After preparing catalyst layer on working electrode and washing the counter and reference electrodes, the electrolytes should be prepared. 0.5 M H2SO4, 0.5 M and 1 M and methanol solutions are made and is exposed to the nitrogen gas to remove the oxygen. After preparing the electrodes and electrolytes, the setup is ready and the electrodes are put into the electrolyte for electrochemical tests.

3. Results and discussion

Cyclic voltammetry is conducted in 0.5 M solution of sulfuric acid to measure the active electrochemical surface area of different synthesized catalysts which shows the active catalytic sites. Fig. 1 shows the voltammetry graph obtained for PtRu/CB and PtRu/CNT. As it is seen, by increasing the voltage in positive direction in forward scan, a peak voltage is occurred at -0.19 V which shows desorption of hydrogen on electro-catalyst surface. On the other hand, increasing the current in negative direction, which is made by decreasing the voltage in reverse scan, shows adsorption of hydrogen on electro-catalyst surface. By calculating the average area under the curve at peak of hydrogen adsorption and desorption, the amount of transferred Colonic load in this process and active electrochemical surface area is obtained for samples. This is an important parameter for finding the amount of using the electrocatalytic property of PtRu alloy and for determining the electrocatalytic activity. The error of calculating the active electrochemical surface area using area under the curve integration technique can be significant at hydrogen adsorption and desorption region, in case of selecting inappropriate double layer region. According to obtained graphs, it can be seen that the sample supported by carbon nanotube has greater peak and under the peak area than the sample supported by carbon black. Using double layer region correction, the amount of active electrochemical surface area for carbon nanotube sample and carbon black sample were calculated 52.3 m^2/g and 27.6 m^2/g, respectively.

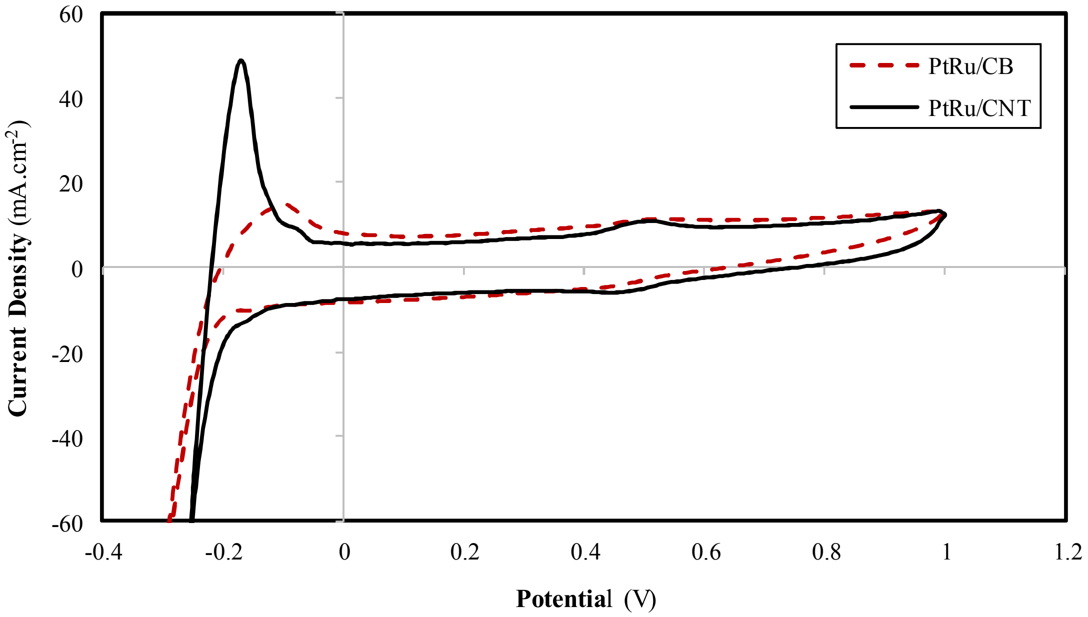

Fig. 1 Cyclic voltammetry test of synthesized samples

Based on Fig. 2, the performance of the electro-catalysts in methanol oxidation reaction is investigated using cyclic voltammetry technique in 0.5 M sulfuric acid and 1 M methanol solution at room temperature. In this analysis, the voltage is varied between -0.3 to 1 V with a scan rate of 50 mV/s. In order to reach the steady state condition, the graph data are saved and reported after 10 cycles. Fig. 2 shows the graph of this analysis for PtRu/CB and PtRu/CNT samples. As it is shown, a peak (I_f) is observed at 0.7 V in forward scan which is related to the methanol oxidation reaction. I_f denotes the electrocatalytic activity and the greater the current intensity produced at peak is, the better the methanol oxidation is and the catalyst has greater activity. One of the effective parameters is active catalyst surface area and it can be expected that the greater the active electrocatalytic surface area is, the greater the peak current intensity is. Another peak (I_r) is observed at around 0.52 V in reverse scan which is related to oxidation of Carbonated Intermediate Species created during forward scan and methanol oxidation. I_f/I_r ratio is used to specify the amount of catalyst resistance to accumulation of poisonous intermediate species, like CO, which are formed during methanol decomposition. This ratio shows part of the Carbonated Intermediate Species that oxidized to CO2 in forward scan. The greater I_f/I_r ratio is, the more effective removing the poisonous intermediate species from catalyst surface has been happened.

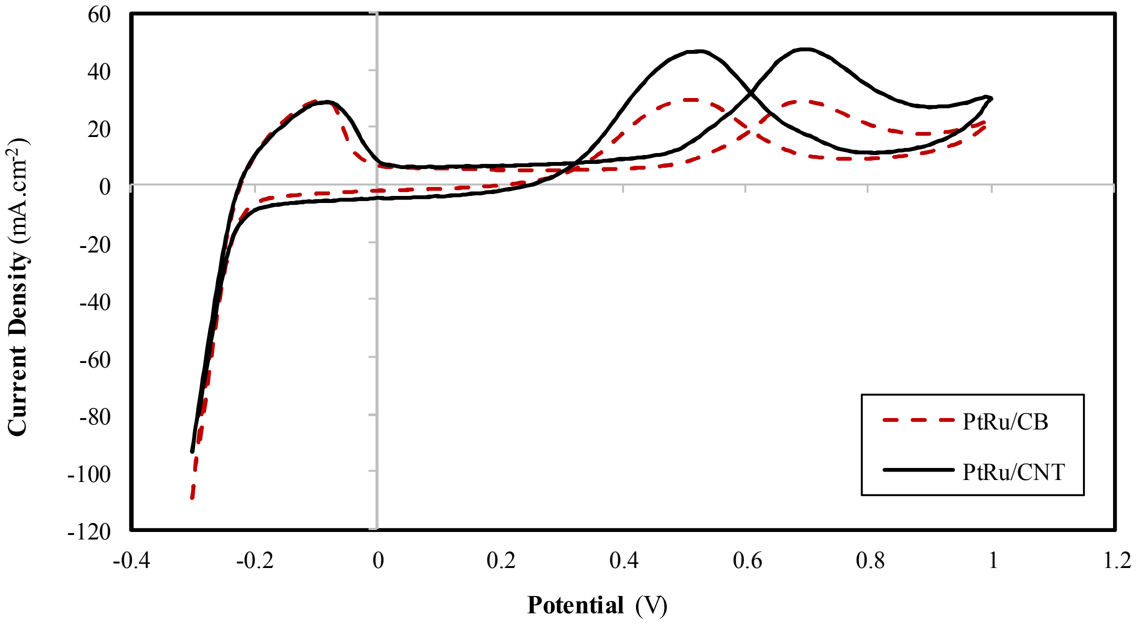

Fig. 2 Cyclic voltammetry test of synthesized samples

According to Table 1, electrocatalytic activity of the sample supported by carbon nanotubes is greater than that of the sample supported by carbon black. The current density obtained from MOR reaction for CNT and CB samples are 47.2 and 29.22, respectively. If/Ir ratio shows that the resistance of the sample supported by carbon nanotubes to poisonous intermediate species is more than that of the sample supported by carbon black.

sampels	I_f (mA.cm^-2)	V_f (V)	I_r (mA.cm^-2)	V_r (V)	I_f/I_r
PtRu/CB	29.22	0.695	29.58	0.51	0.98
PtRu/CNT	47.2	0.7	46.51	0.525	1.014

Table 1 comparison of the electrocatalytic activity, current density and catalytic resistance of the samples

The durability improvement of the electro-catalyst is one of the important research interests in the area of the fuel cell. Due to the continuous oxidation of the methanol at a constant potential, Carbonated Intermediate Species, like carbon monoxide, begin to accumulate on electrode surface area which leads to catalyst poisoning and its performance drop. The long term electrocatalytic activity and stability of the samples were tested and examined using chronoamperometry analysis. In this test, a constant potential of 0.7 V is applied to the electrodes for 1000 s and the current density is plotted as a function of the time. N2 saturated solution containing 0.5 M H2SO4 and 1 M methanol at ambient temperature. Fig. 3 shows the obtained curves using chronoamperometry analysis.

For each sample, curve of current density drops rapidly at first which is due to the production and accumulation of the Intermediate Species in methanol oxidation reaction. Because of higher resistance of PtRu/CNT sample to poisoning species and its better interaction with catalyst, it is observed that it has less current drop compared to PtRu/CB sample at first seconds and after 1000 s, the current density reaches to 21.1 mA/cm2. On contrary, PtRu/CB sample which shows less resistance to the Intermediate Species , the highest current drop is observed at first seconds and finally reaches to 8.3 mA/cm2, abound one third of the CNT supported sample current.

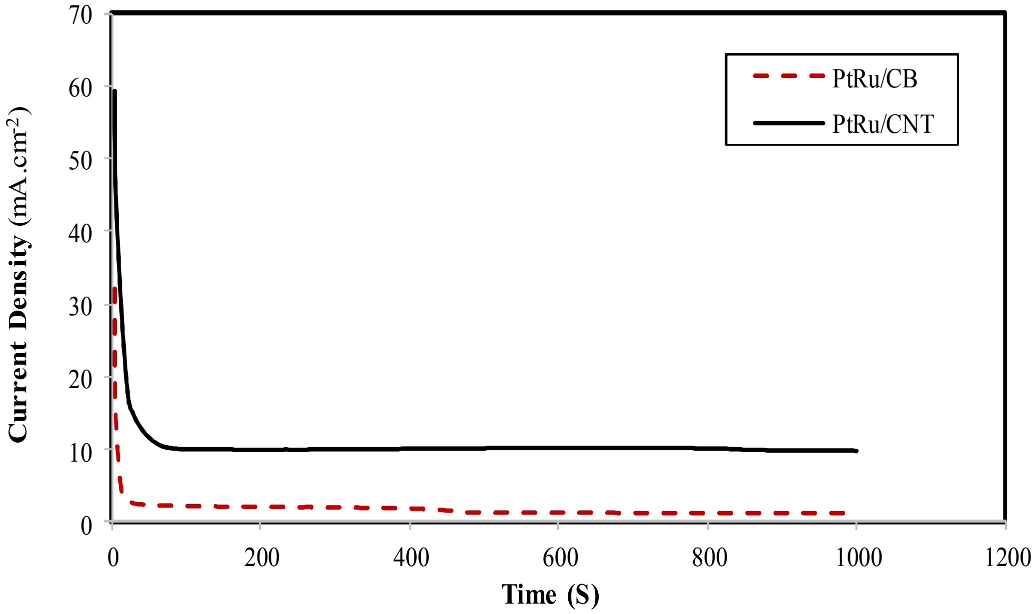

Fig. 3 Chronoamperometry test of synthesized samples

Finally, by fabricating the passive methanol micro-fuel cell, its performance was compared using existing electro-catalysts. For this reason, the micro-fuel cell was tested using two different MEA type based on anode and cathode electrocatalysts with Pt/MWCNT (cathode) and PtRu/MWCNT (anode) support and MEA type based on carbon black supported catalyst (Pt/C (cathode) and PtRu (anode)). The tests were conducted in 3 M methanol solution and the results are shown in Fig. 5 and Fig. 6.

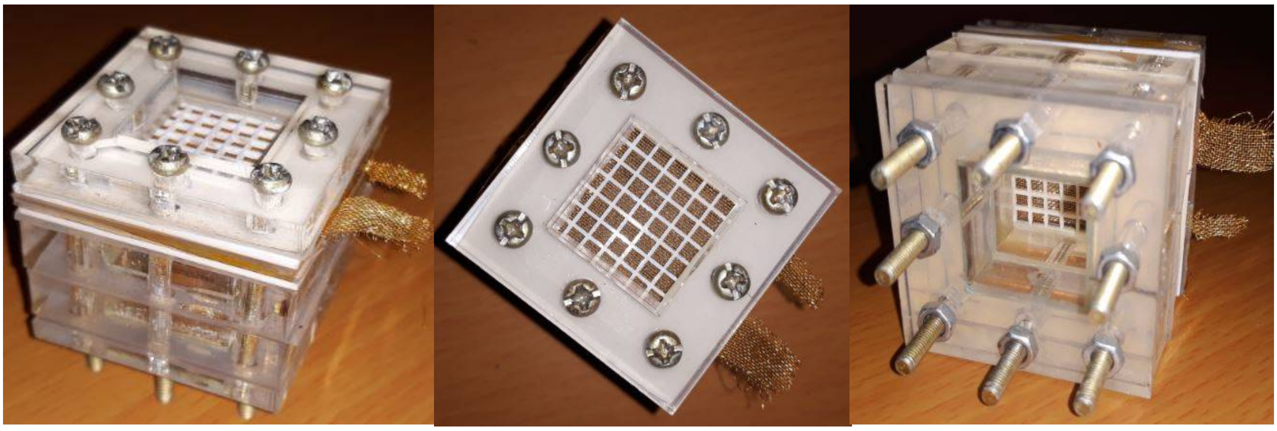

Fig. 4 Schematic view of the fabricated methanol micro-fuel cell

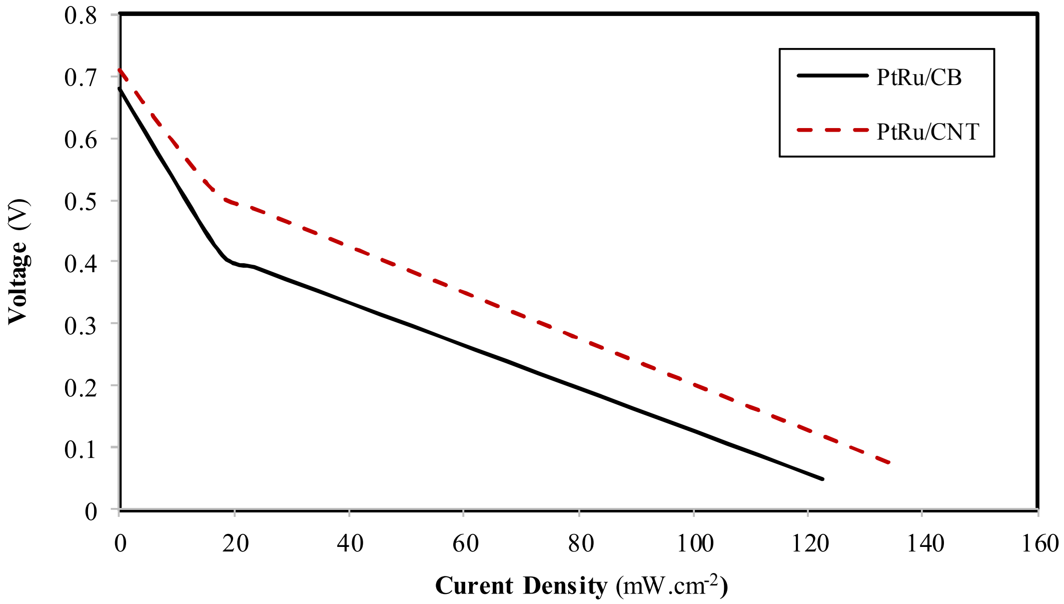

Fig. 5 Electrochemical test of the fuel cell for samples-Voltage graph in terms of current density

By comparing the current-voltage curve of the fuel cell for carbon and nanotube supported samples at low current densities (0-10 mA/cm2)-which is the region related to losses of activation energy and passing of methanol through membrane-a slight decrease in performance drop of the fuel cell is observed. This is due to the activity improvement of the catalyst layer structure as a result of improvement in electrical properties and reactors distribution. This performance improvement has similar effects up to medium power densities (70 mA/cm2). At high power densities (more than 70 mA/cm2), due to increasing the chemical reaction rate, the fuel consumption is increased. Because of less porosity of the catalyst layer structure in carbon supported sample compared to MWCNT supported sample, fueling is weak and voltage drop is higher in carbon supported sample. Therefore, it can be concluded that using carbon nanotubes can lead to decrease in losses due to electrical resistance and mass transfer and also decrease in passing of methanol through membrane. Moreover, using nanotubes doped by nitrogen improved the methanol efficiency throughout the current density which led to significant improvement in performance of the fuel cell.

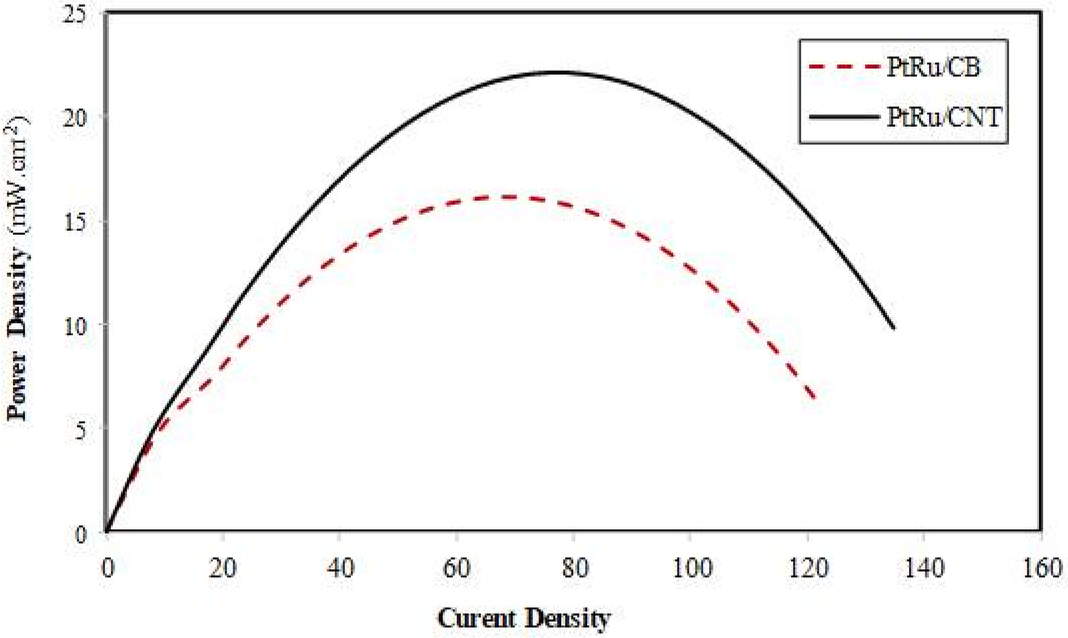

Fig. 5 Electrochemical test of the fuel cell for samples-Power graph in terms of current density

Because of the better dispersion and distribution of the catalyst particles on CNT supported sample surface area, a significant increase in performance of the fuel cell is observed which is due to the increase in catalytic activity of platinum and ruthenium. Increase in activity and efficiency of the catalyst leads to decrease in activation energy, decrease in passing of methanol through membrane and as a result increase in oxidation reactions rate. Hence, losses due to these two phenomena have been significantly decreased and higher performance is observed in comparison to carbon supported catalyst. Table 2 summarizes the results of the tests. Based on the results, the performance of the fuel cell has been increased 5.987 mW/cm2 at maximum power density using carbon nanotubes sample compared to carbon sample.

Table 2 comparison of results of fuel cell maximum output power for different catalysts

Test Temperature	**Cathode catalysts**	**Anode catalysts**	**maximum power density (mW.cm^{-2})**	**supported catalyst**
60 ˚C	**Pt**	**PtRu**	16/133	**CB**
60 ˚C	**Pt**	**PtRu**	22/12	**MWCNT**

4. Conclusion

Based on the tests and analysis conducted in this study, following results have been obtained:

Due to higher specific surface area of the carbon nanotubes compared to carbon black, the other catalyst particles on carbon material decreases and as a result the active electrochemical surface area increases. Based on cyclic voltammetry test in acid solution, the active electrochemical surface area for carbon nanotube sample and carbon black sample using double layer region correction were calculated as 52.3 m2/g and 27.6 m2/g respectively. It was found that the active electrochemical surface area of carbon nanotube supported catalyst is 1.9 times higher than that of the carbon black. Electrocatalytic activity in MOR reaction for CNT sample showed significant increase compared to CB sample which was due to unique properties of the carbon nanotube like high electrical conductivity, greater specific surface area and better interaction with catalyst. In addition, a slight improvement in resistance of CNT electro-catalyst to CO was observed. The resistance to poisonous intermediate species for the CNT supported sample and CB sample were achieved 1.014 and 0.98 respectively. Therefore, due to better resistance and higher electrochemical activity of CNT electro-catalyst in chronoamperometry test, it can show better performance in long term and has more stability and lifetime. Maximum power density for CNT and CB were 22.12 mW/cm2 and 16.133 mW/cm2 respectively which an increase of 5.987 mW/cm2 was obtained using CNT compared to CB. Methanol oxidation onset potential-which is a criterion for kinetic improvement of methanol oxidation reaction-for CNT and CB were 4.4 V and 5.3 V respectively, which shows the better performance of the CNT. Current density in methanol oxidation reaction for carbon black supported sample and carbon nanotube supported sample were 29.2 mA/cm2 and 47.2 mA/cm2. Finally, using carbon nanotubes as catalyst support generally leads to improvement of catalyst layer performance and consequently to increase in output power of the fuel cell. Therefore, using carbon nanotubes in electro-catalyst structure causes better catalytic activity of platinum and ruthenium which leads to performance improvement of the micro-fuel cell.

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