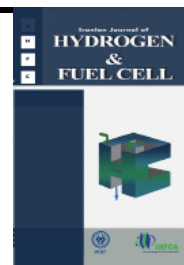


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Preparation and characterization of electrocatalyst nanoparticles for direct methanol fuel cell applications using β -D-glucose as a protection agent

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Abstract

In this study, the activity, stability and performance of carbon supported platinum (Pt/C) electrocatalyst in cathode and carbon supported Pt and ruthenium (PtRu/C) electrocatalyst in the anode of a direct methanol fuel cell (DMFC) were studied. The Pt/C and PtRu/C electrocatalysts were prepared by the impregnation reduction method. The β -D-glucose was used as a protection agent to reduce particle size and improve performance of the prepared electrocatalysts. The prepared electrocatalysts were characterized by using X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. The results of XRD and TEM showed that the average particle size of metals in the prepared electrocatalysts is between 2-3 nm. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry were used to investigate electrooxidation of methanol and electrocatalytic activity of the prepared electrocatalysts. The results showed that the PtRu/C electrocatalyst has better activity in methanol condition due to its smaller average particle size of nanoparticles, superior activity for methanol oxidation and its higher carbon monoxide (CO) tolerance. The single DMFC cell, consisting of protected electrocatalysts, exhibited a 28% increase in peak power density at room temperature, with the maximum peak power density of 22.13 mW cm⁻².

1. Introduction

Direct methanol fuel cells (DMFCs) are attractive choices for energy sources due to their high energy density and operation without pollution [1, 2]. One of

the important parts in DMFCs is the electrocatalyst layer that increases the kinetic of reduction of Oxygen gas in the cathode side and oxidation of methanol in the anode side of the cell [3]. Platinum (Pt) and Pt-based alloys, which are catalytically active in

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an extensive range of temperature, are widely used in DMFC electrocatalyst layer application [4]. In recent years, electrocatalysts deposited on carbon based supports (Vulcan, carbon nanotubes (CNTs) and Graphene) and metal oxide based supports have attracted much attentions in DMFC applications [5]. The best known electrocatalyst for cathode electrode reactions is carbon supported Pt (Pt/C), which can be prepared by several methods such as impregnation, sol-gel, polyol process, microwave irradiation, electroless and electrochemical deposition method [6]. For each method, controlling the nucleation and growth of particles are important parameters to achieve better product performance [7]. Reduction of Pt salts is one of the best methods to prepare Pt electrocatalyst. Borohydride, formaldehyde, ethanol and formic acid are used as reductant agents for reduction reaction [8, 9]. Effects of size distribution and loading of nanoparticles on the performance of the electrocatalyst were investigated [5]. As we know, metal catalytic activity is strongly dependent on some parameters such as particle size, shape, loading and size distribution. Therefore, the Pt particle with suitable loading, appropriate and identical size was used to achieve higher electrocatalytic activity [10]. It was reported that Pt and Pt-based alloys less than 3 nm exhibited the highest mass electrocatalytic activity for the reduction and oxidation reaction [8, 10]. In addition to these parameters, the type of process, condition of operation, and concentration of Pt salts are other parameters that should be controlled [10]. Addition of protection agents such as surfactant, ligands or polymers into the reactions is important to achieve Pt nanoparticles with appropriate size distribution [11]. After the reduction reaction to enhance access of the fuel to catalytic sites, protecting molecules should be removed.

Methanol oxidation performance decreases in the anode electrode of DMFCs due to carbon monoxide (CO) poisoning of the Pt. To overcome this issue, Pt nanoparticles are combined with other nano materials that have high CO tolerance. Ruthenium (Ru) is widely used as a second metal which increases electrooxidation by the bifunctional mechanism

[12, 13]. When Ru combines with Pt to form PtRu alloy, it constitutes oxygenated species at lower potential than Pt, thus simplifies the oxidation of CO to carbon dioxide (CO₂) [14]. To achieve a carbon supported PtRu (PtRu/C) electrocatalyst with the desired performance, similar to a Pt electrocatalyst, various parameters such as particle size, synthesis method, surface composition, and Ru oxidation state must be controlled [15].

In this work, the Pt/C and PtRu/C electrocatalysts were prepared by the impregnation reduction method for DMFC applications. To achieve an electrocatalyst with high performance, better distribution, smaller size, and improve catalytic activity for methanol electrooxidation, electrocatalysts were synthesized with β -D-glucose as the protection agent. Finally, β -D-glucose molecules were removed by washing with deionized water without heating treatment. The structures of the prepared electrocatalysts were confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The electrocatalytic activity of the electrocatalysts was investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry; and lastly, the prepared membrane electrode assembly (MEA) from the synthesized electrocatalysts was tested on DMFC condition.

2. Experimental

2.1. Synthesis of electrocatalysts

The 20 wt% Pt/C electrocatalysts were prepared according to the following procedures: First, appropriate amounts of commercial carbon black (Vulcan carbon XC-72) as primary support material and β -D-glucose as protection agent were mixed in deionized water and the mixture was ultrasonicated for 2 h to form a homogeneous suspension. Then, a certain amount of chloroplatinic acid (H₂PtCl₆·6H₂O) diluted in 20 mL of deionized water was added into the above suspension. The obtained solution was kept under stirring condition for 4 h, followed by tuning

the pH of the ink to 9-10 to increase the effective protection of β -D-glucose under the alkaline condition. Subsequently, an excess of reductant solution (formaldehyde) was added dropwise into the mixture during continuous stirring at room temperature for 8 h. Finally, the suspension was washed several times with deionized water and then the product was dried at 70 °C overnight.

The 20 wt% PtRu/C electrocatalysts (atomic ratio Pt:Ru~1:1) employed in this work were prepared in a single step by an alcohol reduction process using Vulcan XC72 as support, $\text{H}_2\text{PtC}_{16}\cdot 6\text{H}_2\text{O}$ and ruthenium(III) chloride (RuCl_3) as metal sources, β -D-glucose as protection agent and ethanol as reductant solvent. According to this procedure, first, appropriate amounts of carbon black and β -D-glucose were dispersed in 20 mL ethanol for 30 min. Then, 35 mg of RuCl_3 was dissolved in 10 mL of deionized water and the resulting solution was added into 10 mL deionized water containing 69.2 mg of $\text{H}_2\text{PtC}_{16}\cdot 6\text{H}_2\text{O}$. The resulting solution was added into the above suspension and then 160 mL ethanol was added to the mixture. The resulting mixture was treated in an ultrasound bath for 2 h and then submitted to reflux at (80 °C) for 3 h under open atmosphere. After that, the mixture was cooled to room temperature and then centrifuged to separate the electrocatalyst powder. The obtained solids were washed several times with ethanol and deionized water and finally dried in a vacuum oven at 70 °C.

2.2. Physiochemical characterization

The metal contents were determined by inductively coupled plasma (ICP). The measurement was performed by collecting the filtrates during the washing process and determining the loading of metal contents on the carbon support. The crystal structure of electrocatalysts and the average size of nanoparticles were confirmed by XRD. XRD patterns were recorded using an X pert pro Philips Diffractometer with $\text{Cu K}\alpha$ radiation. The TEM (Zeiss EM900) was used to determine the size and distribution of the electrocatalysts.

2.3. Fabrication of MEA

The electrodes for electrochemical characterization were prepared by the following procedure: the electrocatalyst suspension was prepared by using Pt/C or PtRu/C electrocatalyst, 15 wt% polytetrafluoroethylene (PTFE) binder solution, isopropyl alcohol, and a suitable amount of deionized water and glycerol. For preparation of the electrode, the prepared electrocatalyst ink was painted onto a carbon cloth (E-tek, HT 2500-W) and dried in an oven at 80, 120 and 320 °C for 30 min at each temperature. For preparation of MEA, the Nafion 117 membrane was sandwiched between two electrodes (2 mg cm^{-2} metal loading) and then hot pressed under pressure of 80 Kg cm^{-2} at 130 °C for 2 min.

2.4. Electrochemical Measurements

EIS with a frequency range of 0.1 Hz to 100 kHz and voltage amplitude of 10 mV was studied for electrochemical resistance of the prepared electrocatalysts in a solution consisting of 1 M H_2SO_4 and 0.5 M CH_3OH . CV was performed to calculate the Pt/C electrochemical active surface area (EAS) in 1 M H_2SO_4 solution as electrolyte. The methanol electrooxidation reaction on the PtRu/C electrocatalyst was investigated in 1 M H_2SO_4 + 0.5 M CH_3OH solution. The electrocatalytic activity for PtRu/C was estimated using mass specific activity (MSA) and peak potential for methanol electrooxidation. Several cycles of CVs were completed to achieve a stable and reproducible voltammogram. Then, the CV was recorded at a scan rate of 20 mV s^{-1} from the potential of -0.2 V to 1 V with an Ag/AgCl electrode. All of electrochemical measurements were carried out with an Autolab potentiostat/galvanostat and a conventional three-electrode electrochemical cell consisting of Pt wire as counter electrode, Ag/AgCl as reference electrode and a glassy carbon disk electrode with a diameter of 2 cm as working electrode. Before each test, the electrolyte was purged with N_2 for 15 min to de-aerate the system. All of the electrochemical

measurement experiments were tested at ambient temperature. In addition, a future test was conducted to evaluate the stability of the Pt/C and PtRu/C electrocatalysts. These measurements were conducted by chronoamperometry in 1 M CH₃OH in 0.5 M H₂SO₄ solution at 0.69 V on Pt/C and PtRu/C electrocatalysts. The performances of a DMFC single-cell were tested using the FCT 1505 fuel cell testing system (CHINO, Inc., Japan). The 2 M methanol in the anode and O₂ in the cathode were used as fuel with flow rates of 1 and 500 mL min⁻¹, respectively.

3. Results and discussion

3.1. Characterization of electrocatalysts

The content of metals in the electrocatalysts was measured by ICP and the results are shown in Table 1. Table 1 shows the metal mass percentage of Pt/C and PtRu/C electrocatalysts is 20 and 19 wt%, respectively. Fig. 1 gives the XRD patterns of the Pt/C and PtRu/C electrocatalysts.

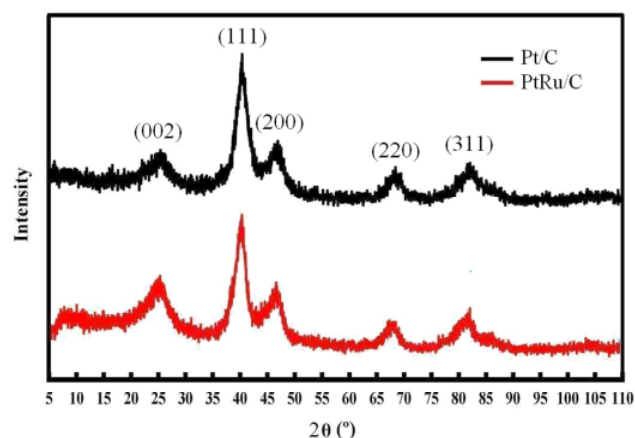


Fig. 1. XRD patterns of the Pt/C and PtRu/C electrocatalysts prepared by impregnation reduction method in presence of protection agent.

The wide diffraction peak at around 25° in both electrocatalysts patterns is attributed to the graphite structure (002) of carbon supports [16]. Four peaks were found for the Pt/C electrocatalyst at 39.8°, 46.4°, 67.8° and 82.2°, corresponding to the (111),

Table 1. Average particle size of nanoparticles in protected electrocatalysts obtained by XRD and TEM and metal loading in electrocatalysts calculated by ICP

Electrocatalyst	XRD	TEM	Pt wt. %	Ru wt. %
Pt/C	3.1 nm	2.4 nm	20	-
PtRu/C	2.9 nm	2.2 nm	11	9

(200), (220) and (311) planes of the face centered cubic phase of Pt nanoparticles respectively. This is consistent with the standard powder diffraction file of Pt (JCPDS No. 04-0802). The Pt with (111) plane showed the highest peak intensity compared to the other Pt planes. This indicates that the samples grow mainly along the (111) plane rather than the other planes, and would produce superior electrocatalytic activity due to improvement of the effective electrocatalyst particles. In the PtRu/C electrocatalyst, a separated diffraction peak for Ru cannot be found because Ru is present in the amorphous phase [17]. Since the PtRu/C electrocatalyst showed diffraction patterns similar to those of the Pt/C electrocatalyst, alloys formation between Pt and Ru in the electrocatalyst cannot be detected [9]. The average particle size of the Pt and PtRu nanoparticles in the prepared electrocatalysts as calculated by the Scherrer formula are 3.1 and 2.9 nm, respectively (Table 1).

TEM images and histograms of the prepared electrocatalysts (with and without protection agent) are presented in Fig. 2, where the black particles are Pt and Ru metals on the carbon substrate. Fig. 2c and d show that Pt and Ru nanoparticles were uniform and well distributed on the Vulcan XC-32 carbon supports surface. The high surface area of Vulcan XC-32 carbon support facilitates the dispersion of Pt and Ru nanoparticles over its surface. As shown in Fig. 2a and b, without the presence of β-D-glucose (protection agent) the nanoparticles somewhat agglomerated on some parts of the carbon support. The results of the particle size of nanoparticles calculated from TEM images are shown in Table 1. The average particle size of the Pt/C and PtRu/C nanoparticles are 2.4 and 2.2 nm, respectively. The images show that the average particle size of

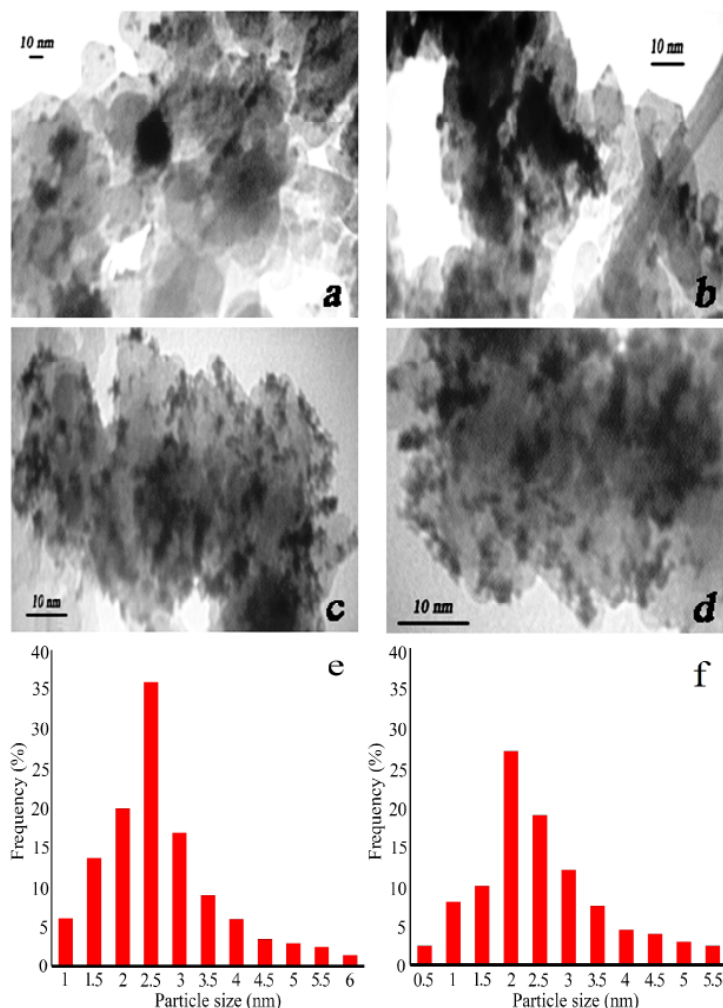


Fig. 2. TEM images of the (a) Pt/C electrocatalyst without protection agent, (b) PtRu/C electrocatalyst without protection agent, (c) Pt/C electrocatalyst with protection agent and (d) PtRu/C electrocatalyst with protection agent and histograms of (e) Pt/C electrocatalyst with protection agent and (f) PtRu/C electrocatalyst with protection agent

nanoparticles decreases with the presence of a protection agent. The interaction between metals and hydroxyl groups of β -D-glucose can stabilize Pt and Ru nanoparticles [18]. The results of Table 1 show that the average particle size of metals calculated by TEM was smaller than those calculated by XRD, but both results showed a similar trend as electrocatalyst.

3.2. Electrochemical Characterization

The electrochemical properties of the Pt/C and PtRu/C electrocatalysts were investigated by CV in a 1 M H_2SO_4 solution at room temperature. The CVs were examined at 20 mV s^{-1} for the PtRu/C

electrocatalysts prepared at 1:1 Pt:Ru atomic ratios under 10 mg of Pt loading. The CVs for electrodes containing Pt/C and PtRu/C electrocatalysts in 1 M H_2SO_4 solution are presented in Fig. 3. The peaks appearing in the region between -0.2 to 0.2 V corresponded to the hydrogen adsorption/desorption process. Around 0.1 V to 0.4 V, the only current that flows is that required to charge the electrolytic double layer. The present peak between 0.4 to 1 V is due to the formation of oxide species [19]. The cathodic peak at around 0.6 to 0.7 V in the reverse scan is due to the reduction of oxide species present in the electro catalyst. The EAS can be estimated through the total

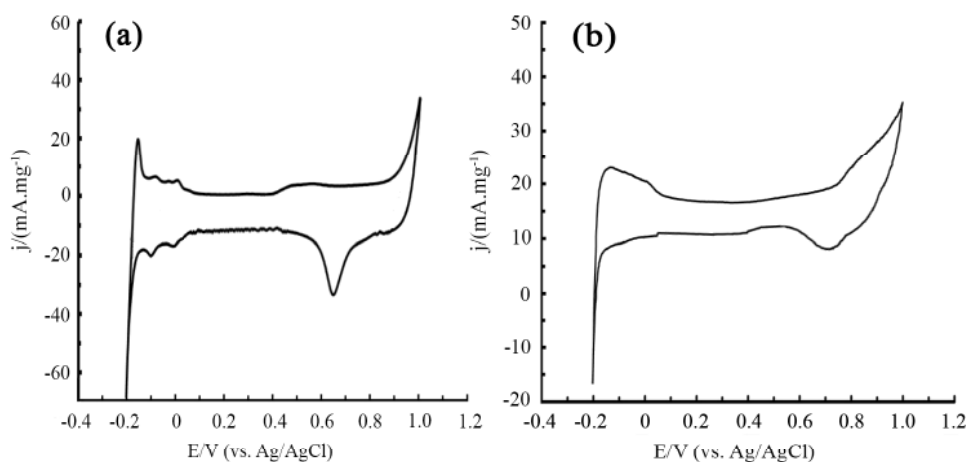


Fig. 3. CVs for protected a) Pt/C and b) PtRu/C electrocatalysts in a 1 M H_2SO_4 solution at a scan rate of 20 mV s^{-1} at 30°C .

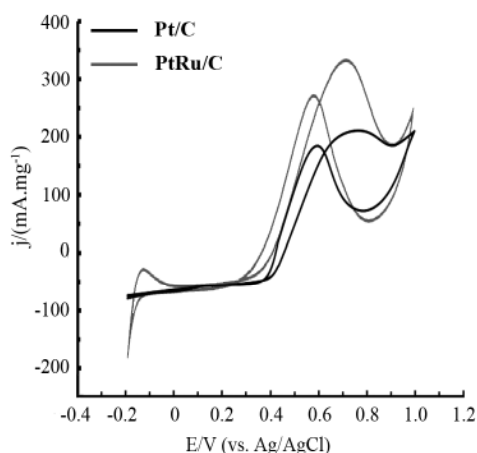


Fig. 4. CVs of methanol electrooxidation on protected Pt/C and PtRu/C electrocatalysts in a 1 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$ solution at a scan rate of 20 mV s^{-1} at 30°C .

amount of charge associated by the hydrogen adsorption/desorption by using the equation:

$$EAS = \frac{QH}{0.21 \times [Pt]} \quad (1)$$

Here, Q_H is the coulombic charge for hydrogen desorption (mC cm^{-2}), $0.21 \text{ (mC cm}^{-2}\text{)}$ is the charge required for the adsorption of the H_2 monolayer on the Pt surface and $[Pt]$ is the platinum loading (0.2 mg cm^{-2}). The EAS for the Pt/C electrocatalyst obtained by this equation is $45.3 \text{ m}^2 \text{ g}^{-1} \text{ Pt}$.

The methanol electrooxidation activity was studied on the prepared electrocatalyst in a solution consisting of $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$ at room temperature to investigate the effect of Ru addition to the Pt/C electrocatalyst. As shown in Fig. 4, the peak at

around 0.7 V in the forward scan can be attributed to the methanol oxidation and the observed peak in the reverse scan can be attributed to the removal of incompletely oxidation intermediate adsorbed on the electrode surface in the forward scan [13]. The ratio of the forward anodic peak (I_f) to the reverse anodic peak (I_b), I_f/I_b , can be used to describe the catalyst tolerance to CO [20]. The methanol oxidation current of the PtRu/C electrocatalyst was higher than that of the Pt/C electrocatalyst, which was attributed to the smaller average particle size of nanoparticles and the higher CO tolerance of the PtRu/C electrocatalyst [21]. As we know, higher I_f/I_b indicates higher methanol electrooxidation activity of the PtRu/C electrocatalyst for DMFC application [20, 21]. The

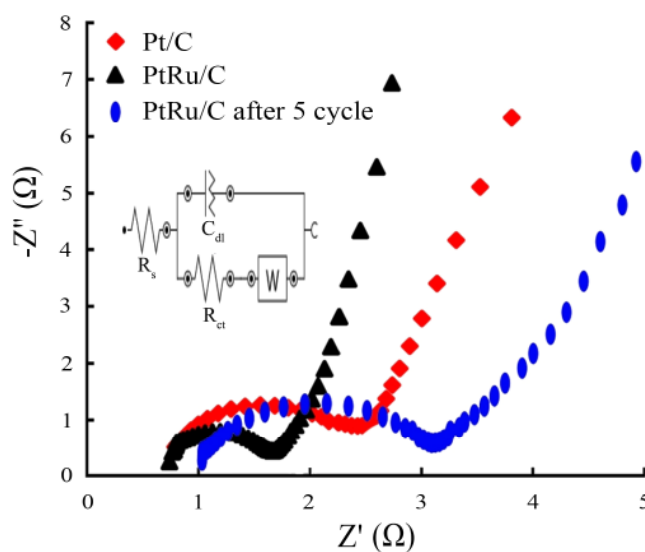
MSA and peak potential for methanol electrooxidation were used to estimate the electrocatalytic activity of the electrocatalysts. The MSA for the electrocatalysts was calculated by integration of the charge density corresponding for methanol oxidation divided by metal loading using the equation:

$$MSA = \frac{Q_{MOR}}{LPtRu} \quad (2)$$

where, MSA is the mass specific activity for methanol oxidation reaction (MOR) (mC mg^{-1}), Q_{MOR} is the charge density for methanol oxidation peak (mC cm^2) and $LPtRu$ is the loading of nanoparticles in the electrode. The peak potential for methanol electro oxidation is 0.7 V and calculated values of MSA for the Pt/C and PtRu/C electrocatalysts are 119 and 203 mC mg^{-1} , respectively. The EIS results of the Pt/C and PtRu/C

electrocatalysts in a solution consisting of 0.5 M H_2SO_4 + 1 M CH_3OH are shown in Fig. 5. It is seen that the Nyquist diagram has two clear parts and two semicircles. The small arc that appears at the higher frequent area is related to electrical conduction via the electrical double layer (C_{dl}) or via geometric boundaries. The second semicircle that appears at the lower frequent area is related to the electrooxidation of methanol.

This result implies that PtRu/C has a good electrical double layer capacitance, which could be explained by the improved dispersion of metal nanoparticles on the surface of the carbon support and its specific surface area. The EIS measurements of the anode electrocatalyst (PtRu/C) were investigated after several cycles of CV. The large arc, shown in Fig. 5, exhibits the slow electrochemical kinetic of methanol dehydrogenation oxidation. This slow kinetics is caused when the adsorbed CO (CO_{ads})



	Pt/C	PtRu/C	PtRu/C after 5 cycle
$R_s (\Omega)$	0.75	0.77	1.1
$R_{ct} (\Omega)$	1.8	0.98	2.1
$C_{dl} (\mu\text{F})$	555	102	476
Estimated error (%)	2.1	2.7	2.82
χ^2	0.11	0.22	0.25

Fig. 5. Nyquist plots of protected Pt/C and PtRu/C electrocatalysts in 1 M H_2SO_4 + 0.5 M CH_3OH solution with voltage amplitude of 10 mV at 30 °C.

blocks further adsorption and the dehydrogenation of methanol, which is released on the surface of the electrochemical electrocatalyst in CV duration. The EIS results were fitted to an equivalent circuit by Nova software and its equivalent circuit was reported in the insert in Fig. 5. The amount of estimated error of real and fitted elements of Nyquist, such as solution resistance (R_s), charge transfer resistance (R_{ct}) and C_{dl} , were monitored in a Table in Fig. 5.

The stable activity of electrocatalysts under potentiostatic conditions is essential for oxidation of methanol in DMFC. Fig. 6 shows the chronoamperometry curves of the prepared electrocatalysts measured in a solution mixture consisting of 0.5 M H_2SO_4 and 1 M CH_3OH at measured in a solution mixture consisting of 0.5 M H_2SO_4 and 1 M CH_3OH at potential of 0.7 V at room temperature. This potential was used due to the oxidation current peak observed in the CV technique. Both electrocatalysts show current degradation with increasing time. The chronoamperometry curves exhibit fast decline at the initial period of time due to the intermediate species which are collected on the surface of the electrocatalyst's nanoparticles. Nevertheless, the PtRu/C electrocatalyst shows a higher initial current and a higher current at the end time in the chronoamperometry curve. The lesser activity loss of the PtRu/C electrocatalyst is due to its smaller average particle size of nanoparticles, superior activity for methanol oxidation and higher CO tolerance [22, 23]. This confirms that the PtRu/C electrocatalyst has better electrocatalytic activity, electrochemical stability, resistance to adsorption of CO and longtime stability in comparison with the Pt/C electrocatalyst [24].

3.3. DMFC Test

Fig. 7 compares the current density-potential (I-V) and power density-current density curves for MEAs comprised of Nafion 117 membrane, Pt/C as the cathode electrocatalyst and PtRu/C as the anode

electrocatalyst at room temperature. As shown in Fig.7, the MEA consisting of protected electrocatalysts has a maximum peak power density of 22.13 $mW\ cm^{-2}$ with a maximum current density of 105.2 $mA\ cm^{-2}$, while the MEA equipped with the electrocatalysts without a protection agent has a maximum peak power density of 17.18 $mW\ cm^{-2}$ with a maximum current density of 91.1 $mA\ cm^{-2}$. The electrocatalysts with a protection agent (β -D-glucose) showed a higher open circuit voltage (OCV) and better performance compared to the electrocatalysts prepared without a protection agent, which is consistent with lower average particle size and better dispersion of electrocatalysts in the presence of β -D-glucose in TEM images. The better dispersion of metal nanoparticles on the surface of Vulcan XC-32 carbon tends to improve the electrocatalytic activity of electrocatalysts.

4. Conclusions

Nanostructured materials are currently of interest as electrocatalysts for DMFCs because of their size effects, high surface area and enhanced kinetics. Pt and PtRu supported on a Vulcan XC-32 carbon electrocatalyst were prepared by impregnation reduction method. Formaldehyde and ethanol were used as a reductant agent for the reduction reaction. Decreased particle size and increased performance of electrocatalysts were shown after the addition of β -D-glucose as a protection agent. The XRD patterns confirmed the formation of the Pt and PtRu nanoparticles in the electrocatalyst. Good dispersion with an average particle size between 2-3 nm of Pt and PtRu nanoparticles on the carbon support was confirmed with TEM images. Results of CV showed that the prepared electrocatalysts have good EAS and MSA for methanol electrooxidation. The PtRu/C electrocatalysts displayed better electrocatalytic activity and electrochemical stability than the Pt/C electrocatalyst due to smaller particle size of nanoparticles, higher CO

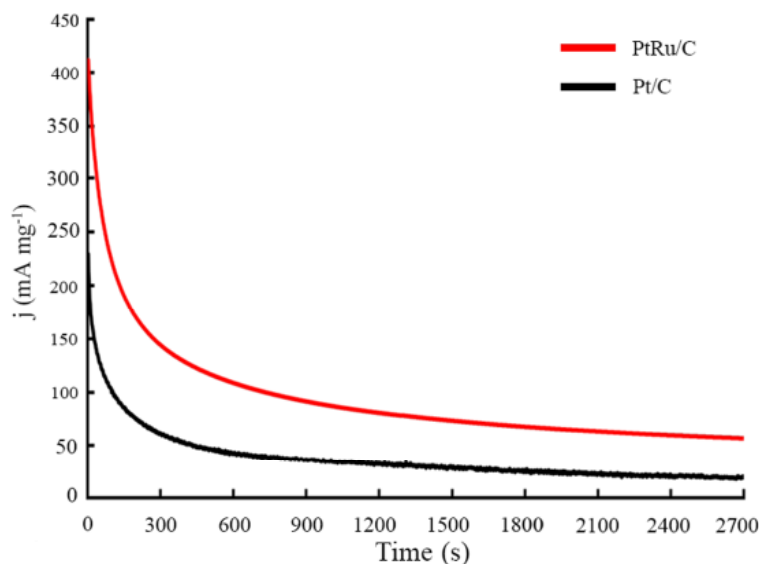


Fig. 6. Chronoamperometric results of protected Pt/C and PtRu/C electrocatalysts in 1 M CH_3OH + 0.5 M H_2SO_4 solution at a potential of 0.69 V at 30 °C.

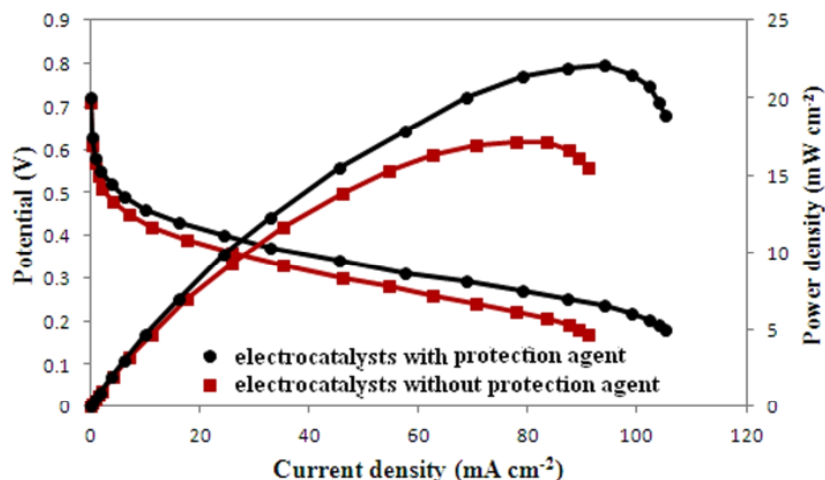


Fig. 7. Current density–potential (I–V) and power density curves of the DMFC assembled with protected and unprotected electrocatalysts and Nafion 117 membrane. The DMFC operated at temperature of 30 °C and ambient pressure with 2 M methanol fuel in anode and pure oxygen fuel in cathode.

tolerance and superior activity for methanol oxidation. The DMFC based on the prepared electrocatalysts and Nafion 117 membranes gave a maximum power density of 22.12 mWcm^{-2} with a highest current density of 105.2 mA cm^{-2} . A literature survey on the performance of electrocatalysts with the same membrane (Nafion 117) is presented in Table 2. It is evident that the power density of the prepared electrocatalysts was comparable to that of commercial and prepared electrocatalyst in other literature.

The electrocatalysts with 20 wt% metal loading showed good electrocatalytic performances in DMFCs.

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Table 2. Comparison of the performance of the DMFCs containing synthesized electrocatalysts and electrocatalysts prepared in other literatures with Nafion 117 membrane at room temperature

Cathode electrocatalyst	Anode electrocatalyst	Power density (mW cm ⁻²)	Ref
Pt/C	PtRu/C	22.13	This work
Commercial Pt/C ^a	Commercial PtRu/C ^b	21.00	[25]
Commercial Pt/C ^c	PtNi/C	19.50	[26]
Commercial Pt/C ^c	PtIrSn/C	20.41	[27]
Commercial Pt/C ^c	PtReSn/C	22.37	[27]
O-PtNi/C	PtRu/C	19.90	[28]

a 40 wt% with 2 mg cm⁻² nanoparticles, E-TEK catalyst

b 20 wt% with 2.1 mg cm⁻² nanoparticles, E-TEK catalyst

c 40 wt% with 2 mg cm⁻² nanoparticles, Johnson Matthey

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