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by Dedi Rohendi

Submission date: 06-Oct-2022 09:42PM (UTC+0700)
Submission ID: 1918263227
File name: zation_of_Electrode_with_Various_of_Pt-Ru-C_Catalyst_Loading.pdf (405.76K)
Word count: 3677
Character count: 18161

Key Engineering Materials
ISSN: 1662-9795, Vol. 840, pp 558-565
doi:10.4028/www.scientific.net/KEM.840.558

Submitted: 2019-05-09
Revised: 2019-07-08
Accepted: 2019-11-11
Online: 2020-04-24

Characterization of Electrode with Various of Pt-Ru/C Catalyst Loading and the Performance Test of Membrane Electrode Assembly (MEA) in Passive Direct Methanol Fuel Cell (DMFC)

Dwi Hawa Yulianti[1,a], Dedi Rohendi[2,3,b*], Nirwan Syarif[2,3,c] and Addy Rachmat[2,3,d]

[1]Master Degree of Programme Chemistry, Faculty of Mathematic and Natural Sciences, Universitas Sriwijaya, Palembang, South Sumatera, Indonesia

[2]Chemistry Department, Faculty of Mathematic and Natural Sciences, Universitas Sriwijaya, Ogan Ilir, South Sumatera, Indonesia

[3]Center of Research Excellent in Fuel Cell and Hydrogen, Universitas Sriwijaya. Palembang, South Sumatera, Indonesia

[a]dwihawayulianti@gmail.com, [b]rohendi19@unsri.ac.id, [c]nsyarif@unsri.ac.id, [d]addy.tea@gmail.com

Keywords: Catalyst loading, Pt-Ru/C, methanol, OCV, DMFC

Abstract. Membrane Electrode Assembly (MEA) is the most important component in fuel cell devices. Electrodes composing MEA greatly determine the performance and durability of its application in passive Direct Methanol Fuel Cell (DMFC). Fabrication and characterization of electrodes with various loading Pt-Ru/C catalysts and their application to DMFC have been carried out. The XRD characterization results indicate the presence of C atoms which are indicated by the appearance of peaks at angles 2θ = 25°-30°. In areas, 44.4° and 45.1° indicate the presence of Ru even with low intensity and platinum in the area of 54.67°, 39.86°, 54.736°, 39.88°, and 68.3°. The highest ECSA value and electrical conductivity and low resistance showed the best catalytic activity possessed by electrodes with the loading of Pt-Ru/C catalyst 10 mg/cm^2. MEA with a catalyst loading of 8 mg/cm^2 is known to have a fairly large initial voltage before the load is given based on the results of Open Circuit Voltage (OCV) measurements. The MEA performance was observed based on I-V and I-P performance tests using the SMART2 WonAtech Fuel Cell Test Station on passive DMFC stacks with 3 M methanol as fuel. The best MEA shown in MEA with catalyst loading is 10 mg/cm^2 because it can maintain and achieve a voltage and power density that is quite higher than other MEAs in each load increase in the form of current density.

Introduction

Energy needs continue to increase along with technological advancements [1]. The biggest energy consumption in 2015 was in the household sector reaching a figure of 38% and industry and services by 29%, followed by transportation by 27% [2]. This is very worrying about the stability between energy production and consumption which has become the primary need of the world. One energy source that is still widely used, namely fossil energy. Its limited availability and impact on the environment such as carbon emissions are a major problem in the use of energy-producing fuels [3]. One solution to this energy problem is to switch to new renewable fuels. Hydrogen and alcohol can be an alternative that has great potential as a producer of environmentally friendly electrical energy [4].

One technology with hydrogen or alcohol-based fuel is a fuel cell. Fuel cells are classified as environmentally friendly energy-producing devices and are predicted to be one of the promising future energy sources because they have high efficiency and minimal emissions. One type of hydrogen and the alcohol-based fuel cell is the Proton Exchange Membrane Fuel Cell (PEMFC) and DMFC. However, DMFC devices have an advantage in operation because the fuel used is a solution instead of gas. The electrical energy produced in the fuel cell is the result of chemical reactions from fuels (hydrogen or alcohol) and oxygen into electrical energy [5].

The use of catalysts on electrodes generally uses a mixture of catalyst Pt with other transition metals such as Ru. The use of Ru is intended to minimize the use of Pt and increase resistance to carbon monoxide poisoning [6]. One of the most important components in DMFC devices is MEA, which acts as a place for reactions that convert chemical energy in fuel to electricity electrochemically [7]. An important component that supports the performance of the fuel cell is MEA, which is the place to convert fuel (hydrogen/alcohol) into electrical energy through a catalytic process [8]. MEA consists of the cathode (the site of the reduction reaction) and the anode (place of oxidation) and the electrolyte membrane in the form of a Nafion which is flanked by both electrodes [9]. Much attention is paid to getting MEA which has high current density and durability due to its very important functions. The thing that needs to be studied to produce high-performance MEA is the content and type of catalyst and the method of making it.

Experimental Section

Pt-Ru/C catalyst was moistened with water then dissolved using isopropyl, Polytetrafluoroetylen (PTFE) and Nafion stirred in ultrasonic for 15 minutes to form an ink. Furthermore, the catalyst ink is sprayed on the surface of the Gas Diffusion Layer (GDL) in a horizontal and perpendicular direction. GDL is made from carbon paper by having a surface area of 16 cm^2 which has been coated with a mixture of carbon Vulcan XC-72, PTFE, ammonium bicarbonate, and isopropyl called Micro Porous Layer (MPL). The GDL coated with a Pt-Ru/C catalyst acts as an electrode on the anode side. The same procedure is carried out for cathodes with Pt/C catalysts. Electrode making composition can be seen in Table 1.

Table 1. Composition of fabrication GDL and electrodes

Loading Pt-Ru/C	**Units** (mg/cm^2)	**GDL**	**Anode 1** (2)	**Anode 2** (4)	**Anode 3** (6)	**Anode 4** (8)	**Anode 5** (10)	**Cathode** (5)
Carbon Vulcan XC72	g	0.576	-	-	-	-	-	-
Isopropil Alkohol	mL	14.4	3.84	7.68	11.52	15.36	19.2	9.6
PTFE	wt%	0.288	0.032	0.064	0.096	0.128	0.16	0.08
Ammonium Bicarbonat	g	0.288	-	-	-	-	-	-
Pt-Ru/C	g	-	0.096	0.192	0.288	0.384	0.48	-
Pt/C	g	-	-	-	-	-	-	0.24
Nafion solution	wt%	-	0.1704	0.3408	0.5112	0.6816	0.852	0.426

Electrodes were characterized and analyzed using XRD to see the presence of constituent atoms, testing electrochemical properties with the CV and Electrochemical Impedance Spectroscopy (EIS) methods carried out using Potentiostat/Galvanostat Autolab PGSTAT204 Metrohm. Then MEA was made by sandwiching the Nafion-117 membrane with both electrodes and pressed using a hotpress pressurized at 2000 psi at 350 °C for 3 minutes.

Determination of MEA performance on various catalyst loading was tested by SMART2 WonAtech Fuel Cell Test Station on one DMFC passive cell with 3 M methanol solution as fuel by observing the ability of MEA to maintain power voltage and density in each addition of current density that is implemented as a load.

Results and Discussion

Characterization of electrodes using X-Ray Diffraction (XRD). The existence of atoms can be known based on XRD characterization by the appearance of peaks in area 2θ according to the characters of each atom. The results of X-ray diffractometer measurements on Pt/C and Pt-Ru/C electrodes from the spraying method are shown in the Fig. 1.

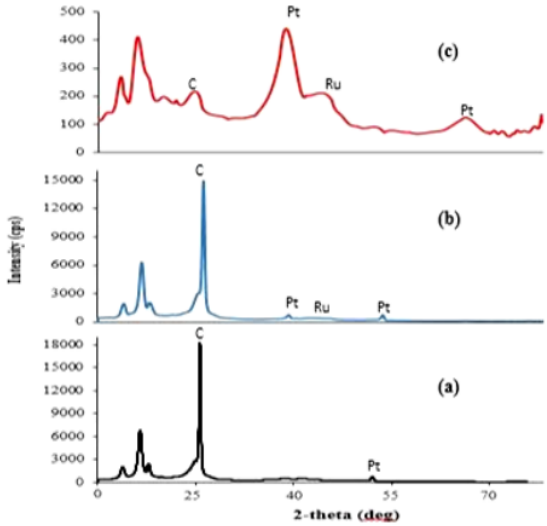

Figure 1. Results of XRD measurements on electrodes with method spraying (a) Pt/C (b) Pt-Ru/C 2 mg/cm^2 (c) Pt-Ru/C 8 mg/cm^2

Based on the results of X-ray diffractometer measurements, the diffractogram difference between electrodes with Pt/C and Pt-Ru/C catalysts. Fig. 1 (a) and (b) show sharp peaks at 20°-30° which are regions of C atoms (JCPDS No.01-1194) [10]. Fig. 1 (b) forms peaks that appear in the area of 39.86° and 54.736° which indicate the presence of Pt and appears at 44.4° with very low intensity indicating Ru atoms, while in Fig. 1 (c) peak of Pt appears in the field of 39.88° and 68.3° and Ru at 45.1°. The existence of Ru as a transition metal has an impact on decreasing intensity due to interactions between atoms. The interaction between Ru and Pt causes a decrease in the length of the interatomic bonds because Ru has a smaller atomic radius [11]. At position 2θ = 12°-20° there is a diffraction peak which indicates that the peak is PTFE and Nafion from a catalyst mixture which is made where sharper peaks show PTFE content while a wider peak and has a lower intensity shows Nafion contents [12].

Characterization of electrochemical properties of electrodes by CV methods. The electrochemical properties of Pt/C and Pt-Ru/C electrodes were analyzed quantitatively using the CV method by measuring current voltage and density using the Potentiostat Autolab Metrohm PGSTAT204. This measurement also involves 3 electrodes in the form of a Reference Electrode (RE), Counter Electrode (CE), and the Working Electrode (WE). The Ag/AgCl electrode acts as a reference electrode and the counter electrode used is platinum (Pt) [13].

Electrode performance measurement using CV method was carried out using a scan rate of 25 mV/s with 1 M sodium hydroxide solution as an electrolyte. The voltammogram curve shows a reversible reaction with the formation of an anodic peak (upper curve) and cathodic peak (bottom curve). A voltammogram for a reversible reaction will produce two peak currents, namely in the cathodic current and anodic current as shown in Fig. 2.

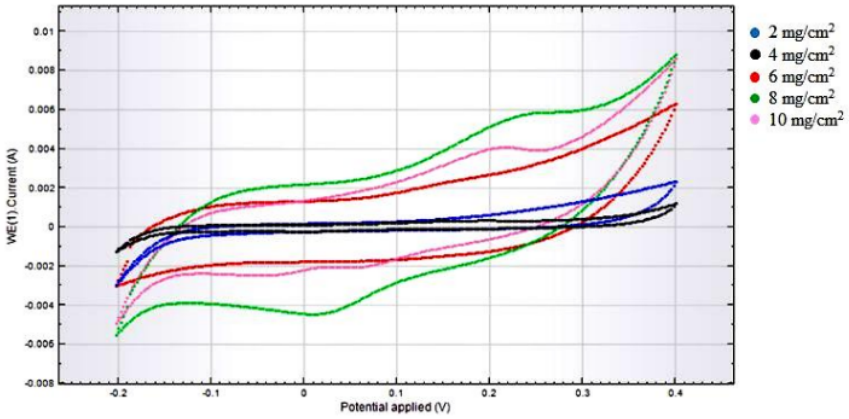

Figure 2. The combined CV curve of electrodes that contain Pt-Ru/C catalyst with various loading at scan rate 25 mV/s

Fig. 2 shows the difference in anodic and cathodic peaks at each electrode. Shift of anodic and cathodic peaks for Pt-Ru/C oxidation and reduction reactions. Negative anodic oeak shifts only show low energy for electrode oxidation [11, 14]. Therefore, electrodes with a catalyst load of 10 mg/cm^2 only require low energy in oxidation and reduction reactions.

Measurements using CV method carried out to determine the catalytic activity of Pt-Ru/C electrodes. These test results can then be used to determine the electrochemical surface area (ECSA) of catalyst in the electrode. The catalytic activity analyzed in ECSA measurements is the number of active sites occupied by each proton on the electrode surface [15]. The results of ECSA measurements are shown in Table 2.

Table 2. The results of ECSA analysis on Pt-Ru / C electrodes

No.	Catalyst loading of Pt-Ru/C (mg/cm^2)	ECSA (cm^2/mg)
1.	2	187.523
2.	4	57.366
3.	6	6.0801
4.	8	288.386
5.	10	373.601

According to Table 2 it can be seen that the Pt-Ru/C electrodes with loading of catalyst 4 mg/cm^2 and 6 mg/cm^2, shows lower ECSA values. This indicates that the catalytic ability of the catalyst from the combination of Pt and Ru also influences the ECSA value of the electrode. In this study, it was found that electrodes with loading of catalyst 10 mg/cm^2 have the best value compared to other electrodes.

One of the factors that influence the value of the electrode catalytic activity is the substrate or carbon matrix in the catalyst. Pt-Ru catalysts are distributed in the carbon matrix in the form of Pt-Ru/C. The more evenly distributed catalyst in carbon, the more active the catalyst site. This is because the large surface makes the Ru metal be distributed between the pore gaps of the carbon and spread evenly on the surface. The amount of catalyst loading does not necessarily affect the catalytic active area, because catalyst buildup can cause the active area of the catalyst to decrease [16].

EIS analysis. The electrochemical characterization of electrodes was carried out using the Potensiostat/Galvanostat Autolab PGSTAT204 Metrohm device using the method of EIS. This EIS method is used to analyze the electrochemical performance of electrodes that will produce data from

the results of sample responses to the given frequency range in the form of real impedance (Z') and imaginary impedance (Z"). If plotted between Z' and Z" the Nyquist curve will be generated as shown in Fig. 3. The frequency range used in the test is 0.1 Hz-100 kHz.

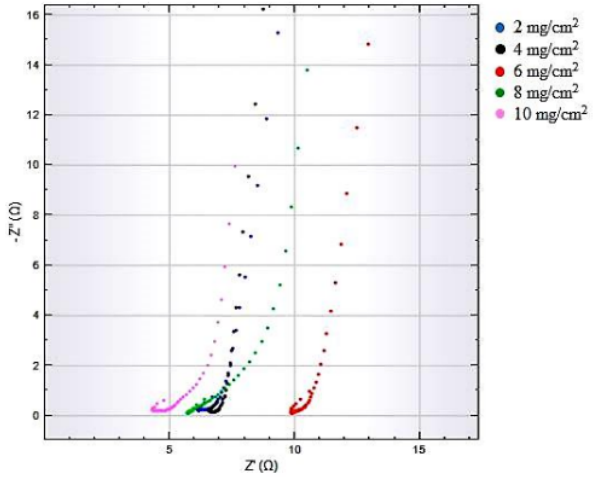

Figure 3. Nyquist electrode plot with various loading of catalysts

Based on the EIS measurement results, the impedance curve is shown as in Fig. 3, where the average of the three electrodes measured has a fairly low impedance value. Pt-Ru/C 2 mg/cm^2 electrode has a real resistance value of 6.268 Ω, Pt-Ru/C 4 mg/cm^2 of 6.675 Ω, Pt-Ru/C 6 mg/cm^2 of 9.965 Ω, Pt-Ru/C 8 mg/cm^2 of 5.786 Ω, and Pt-Ru/C 10 mg/cm^2 of 4.315 Ω. These data indicate that Pt-Ru/C 10 mg/cm^2 is a better electrode than others because it has a lower resistance value. Low resistance values indicate high conductivity. This can be proved by the calculation of conductivity [17, 18]. Conductivity calculations are done by interpreting the pattern obtained from the fitting, which will get value Z_R (real total resistant) and then calculate conductivity through the equation (1):

$$\sigma = \frac{L}{R \cdot A} \quad (1)$$

where: electrical conductivity (σ), sample distance (L), resistivity (R), and surface area (A) [19].

Electrical conductivity analysis. Measuring the electrical conductivity value of Pt-Ru/C electrodes from the spraying method in several variations of Pt-Ru/C catalyst loading is to see the ability of the electrodes to conduct electricity. The results of this electrical conductivity test also determine the ability of the electrode related to its application to the fuel cell. The conductivity value was obtained from the measurement of Pt-Ru/C electrodes connected to the autolab potentiostat by the EIS method and fitting in the Nyquist plot so that the data obtained as in Table 3.

Table 3. Results of fitting Nyquist curves and conductivity

No.	Sample [mg/cm^2]	Impedance Parameters		Electrical Conductivity [S/cm]
		Rp [Ω]	Rs [Ω]	
1.	2	2.3891	5.4704	3.58 x 10^{-4}
2.	4	2.3224	9.7353	2.59 x 10^{-4}
3.	6	7.1454	3.0408	3.37 x 10^{-4}
4.	8	5.6062	4.1715	3.84 x 10^{-4}
5.	10	1.6195	4.5275	6.61 x 10^{-4}

Preparation and testing the performance of MEA in passive DMFC. The fabricating of MEA was carried out by combining the Nafion 117 membrane which was activated with the cathode and anode at 135 °C hot press, 2000 psi pressure for 3 minutes. The MEA made from electrode with the various loading of Pt-Ru/C catalysts at anodes and the constant catalyst loading of cathodes that containing Pt/C at 3 mg/cm^2.

MEA performance measurement. Measurements of Open Circuit Voltage (OCV) is intended to see MEA performance before being given a load. OCV shows the initial voltage value of the electrode. The higher the OCV, the better the MEA's performance is expected. When before the load is given, the electrode has a stored initial potential that interacts with the methanol fuel source, this value is then read on the SMART2 Fuel Cell Test System as an initial voltage value (OCV) of the electrode. The OCV value of each Pt-Ru/C catalyst load is shown in Fig. 4.

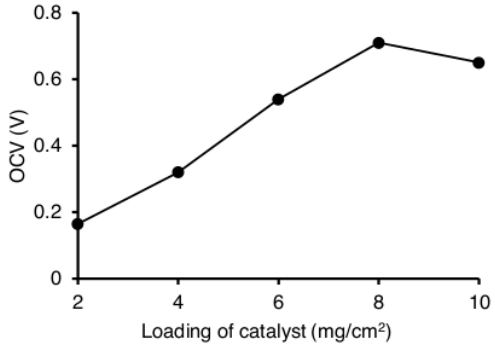

Figure 4. Value of OCV with the variation of Pt-Ru/C catalyst loading

Based on Fig. 4, it can be seen that the largest OCV is produced from MEA with a Pt-Ru/C catalyst loading of 8 mg/cm^2 compared to MEA with a catalyst loading of 10 mg/cm^2. This shows a greater interface barrier in MEA with catalyst linking of 10 mg/cm^2 so that the value of OCV possessed is lower compared to MEA with the loading of 8 mg/cm^2 Pt-Ru/C catalyst. However, the value of OCV is not a major parameter in determining MEA performance. MEA performance can be determined based on the I-V and I-P performance tests.

Performance test of MEA with various catalyst loading. MEA performance testing was carried out in the form of flows using 3M methanol as fuel in the DMFC stack. The following reactions occur in DMFC cells:

$$\text{Anode : } CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$
$$\text{Cathode: } 1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$
$$\text{All reaction: } CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$$

Methanol affects the redox reaction that occurs on the anode and cathode side. Cross over can occur causing a decrease in a performance marked by the appearance of heat on the DMFC stack [20]. Comparison of MEA performance with variations in loading Pt-Ru/C catalysts can be seen in Fig. 5.

Fig. 5 shows the relationship between current density, voltage, and power density. The greater the voltage applied, the greater the power density produced. This is because power is a product of voltage and current density. The best performance is owned by MEA by loading a catalyst of 10 mg/cm^2 seen from the I-V performance curve that can maintain voltage after being given a load in the form of increasing current density. In addition, the I-P performance curve also shows the greatest power density achieved by MEA by loading 10 mg/cm^2 of catalyst at 3.55 mW/cm^2. Thus, MEA with the best catalyst loading is shown in catalyst loading of 10 mg/cm^2 which is also supported by ECSA values, electrical conductivity, and resistance.

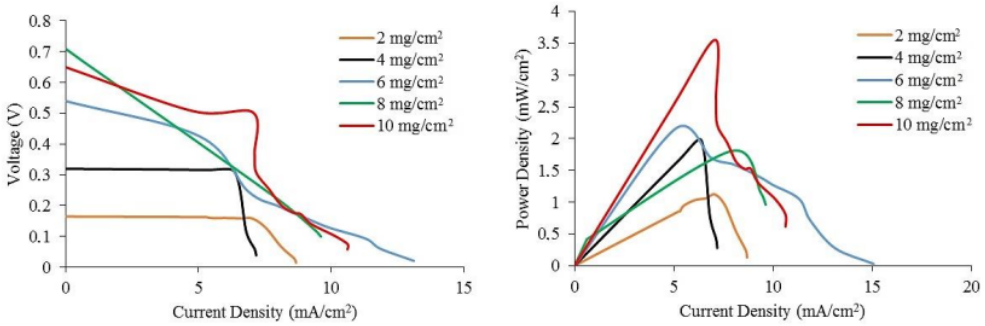

Figure 5. Relationship between current density to voltage and power density

Summary

The highest ECSA value and electrical conductivity and low resistance determine the best catalytic activity possessed by electrodes with loading of Pt-Ru/C catalyst 10 mg/cm^2. MEA with catalyst loading of 8 mg/cm^2 has a greater OCV value. However, the best MEA performance in MEA with catalyst loading is 10 mg/cm^2 because it can support and achieve a high enough voltage and power density to increase other MEAs in the form of current density on the passive DMFC stack based on I-V and I-P performance tests.

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