

Performance Test of Membrane Electrode Assembly in DAFC using Mixed Methanol and Ethanol Fuel with Various Volume Comparison

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Abstract

Direct Alcohol Fuel Cell (DAFC) performance is influenced by electrocatalysis reactions that occur in Membrane Electrode Assembly (MEA). In this study, MEA was made with Pt-Ru/C (anode) and Pt/C (cathode) catalysts. The results of the electrode characterization with XRD showed a carbon peak at 26.63° and Ru at 40.58°. Based on the results of Cyclic Voltammetry (CV) measurements, the Electrochemical Surface Area (ECSA) electrode value is known to be 373.601 cm²/mg. Meanwhile, the impedance value is 4.315 Ω and the electric al conductivity value is 6.61x10⁻⁴ S/cm. MEA testing using MeOH 3 M fuel produces Open Circuit Voltage (OCV) of 0.650 V. Meanwhile, MEA performance testing uses a mixture of methanol and ethanol 2 M in loading conditions obtained the best mixture of fuel composition is methanol: ethanol = 90:10 with a maximum power density of 4.34 mW/cm² and is able to maintain the voltage at 0.649 V under conditions of 6.875 mA/cm². The results also showed that the volume of ethanol which was too high resulted in a decrease in cell performance in the fuel mixture caused by the competition of adsorption between competing methanol and ethanol occupying the active site of the catalyst.

Keywords: DAFC, fuel cell, Pt-Ru/C, ethanol, methanol, Open Circuit Voltage

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INTRODUCTION

Fuel cell is one of the new renewable energy which is predicted to be a very promising alternative technology for the future. Fuel cell has advantages in its ability to produce electrical energy and can also minimize emissions so it is safe for the environment [1]. The type of fuel cell that has the ease of operation and use of fuel is DAFC [2,3].

DAFC is divided into two types, namely Direct Methanol Fuel Cell (DMFC) and Direct Ethanol Fuel Cell (DEFC). The difference between them is the fuel used. DMFC uses methanol and DEFC fuel using ethanol. Methanol and ethanol which are used as fuels have advantages and disadvantages of each. Methanol has a good ability in improving fuel cell performance but is toxic to the environment [4]. Meanwhile, ethanol is lower in performance than methanol but many natural ingredients can produce ethanol so that its availability is abundant in nature [5].

One of the most important parts of DAFC is MEA which is the place where electrochemical conversion of fuel alcohol and oxygen and become electricity as the

main product and water and CO₂ as side product [6]. The most important part of MEA is the electrode containing the catalyst.

Platinum and ruthenium are widely used as catalysts in fuel cells (especially fuel cell fueled with alcohol) because they can minimize poisoning of carbon monoxide or carbon dioxide which can inhibit and reduce fuel cell performance [7].

This study used the Pt-Ru/C catalyst in the Pt/C anode section in the cathode section and varied the volume ratio of methanol and ethanol 2 M to determine the best MEA performance on DAFC devices.

MATERIALS AND METHODS

Manufacturing Gas Diffusion Layer (GDL) was carried out by mixing carbon Vulcan 0.576 g, 14.4 mL isopropyl, 0.288 wt% Polytetrafluoroetylen(PTFE) and ammonium bicarbonate then stirring in ultrasonic homogenizer to produce ink and sprayed on the surface of the carbon paper. Furthermore, the catalyst layer was made by mixing 0.48 g of Pt-Ru/C catalyst with a little water and 19.2 mL of added isopropyl. Then, 0.852 wt% of the Nafion solution was added and 0.16

wt% PTFE was stirred for 15 minutes using an ultrasonic homogenizer to form an ink. Catalyst ink sprayed on the surface of the GDL which has a surface area of 16 cm² forms the anode. The same procedure is carried out for cathodes with Pt/C catalysts.

Electrodes were characterized and analyzed using XRD to show the degree of crystallinity of the constituent compounds. Testing of electrochemical properties using the cyclic voltammetry and Electrochemical Impedance Spectroscopy (EIS) methods was carried out using the Metrohm Autolab PGSTAT128N.

MEA was made by attaching the anode and cathode to both sides of the Nafion 117 membrane with an emphasis of 2000 psi using heat stress at 135° for 3 minutes. MEA's performance on various loading catalysts was tested by SMART2 Fuel Cell Test Station on single active DAFC cells using a mixture of methanol and ethanol 2 M.

RESULTS AND DISCUSSION

Electrode Characterization using XRD

The presence of elemental or compound particles can be analyzed using XRD which is indicated by the diffraction angle (2θ) and the shape and intensity of the diffractogram peak. The results of X-ray diffractometer measurements on Pt/C and Pt-Ru/C electrodes are shown in figure 1.

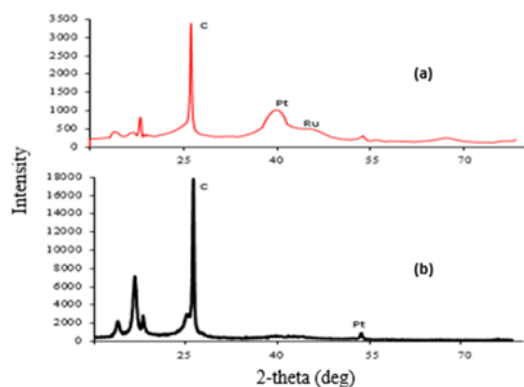


Figure 1. XRD Measurement Results (a) Pt-Ru/C anodes and (b) Pt/C

Figure 1 shows the appearance of peaks on Pt-Ru/C and Pt/C electrodes. Figure 1 (a) shows the peak of C in the region of 26.636° and 40.58° which indicates the peak of Pt [8]. Meanwhile, in figure 1 (b) shows the peak of C at region 26.703° and Pt at 54.67°. In addition, peaks also appear in the area around 12° -20° which indicates the peak of PTFE and nafion [9]. Decreasing Pt atomic intensity is seen in the results of XRD Pt-Ru/C electrodes. This occurs due to the addition of Ru which indicates interatomic interaction of Ru metal and Pt [10].

Electrode Testing using the Cyclic Voltammetry (CV) method

Testing of Pt-Ru/C electrodes using the CV method aims to determine the electrochemical properties of the electrodes. The electrochemical properties can be determined from the value of the Electrochemical Surface Area (ECSA) based on anodic and cathodic peaks that appear in the form of a voltammogram curve. CV measurements were carried out using the Autolab Metrohm PGSTAT128N Potentiostat / Galvanostat tool with a search rate of 25 mV/s. The measurement involved 3 electrodes namely the working electrode (Pt-Ru/C), the reference electrode (Pt) and the reference electrode (Ag/AgCl) and 1 M sodium hydroxide solution as the electrolyte [11]. The result of CV measurement of Pt-Ru/C anode is shown in Figure 2.

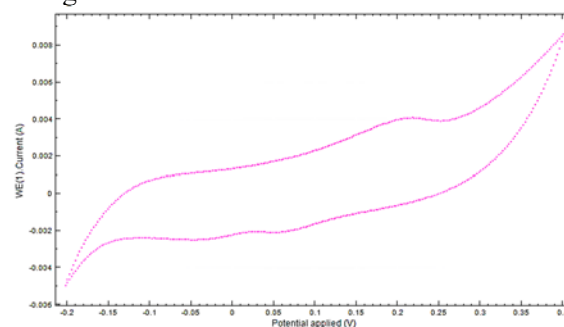


Figure 2. Pt-Ru/C electrode Voltammogram with a search rate of 25 mV/s

The voltammogram curve shows the presence of anodic and cathodic peaks on the measurement results of CV. Anodic peaks appear at a potential of 0.207 V. While the cathodic peaks appear in the area of -0.033 V, the appearance of anodic and cathodic peaks indicates the release and capture of electrons so that redox reactions occur. Shifting the anodic peak to the right shows the amount of energy needed to react [10]. The catalytic activity of Pt-Ru/C electrodes can be determined from the ECSA value. ECSA values can be calculated based on anodic and cathodic peaks that appear on CV measurements. The ECSA value of Pt-Ru/C electrodes is 373.601 cm²/mg. The ECSA value shows the number of catalyst active sites distributed into the carbon matrix on the GDL surface [12].

Testing of Electrochemical Impedance Spectroscopy (EIS) and Electrical Conductivity

The EIS method is performed to see the impedance values displayed on the Nyquist curve. The resulting data is the electrode response to real (Z') and imaginary (Z'') impedance values [13]. This analysis shows the interaction of electrodes with the frequency range used in the test is 0.1Hz - 100kHz.

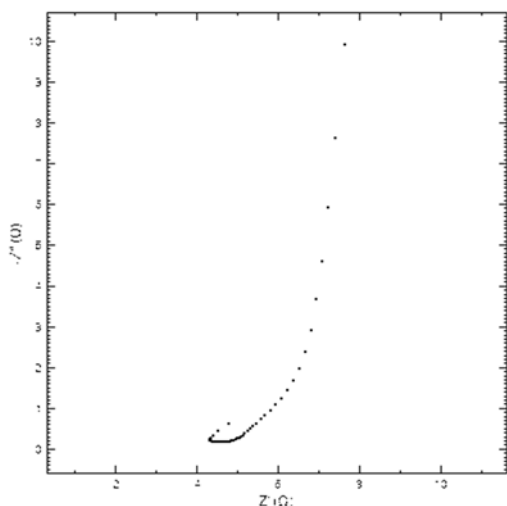


Figure 3. Nyquist Curve Pt-R/C electrodes

Figure 3 shows the results of EIS measurements in the form of the Nyquist curve. Based on this test, the real impedance value of the Pt-Ru/C electrode is known to be 4.315 Ω. In addition, the shape of the Nyquist curve also shows corrosion resistance. The more curved shape of the curve indicates greater corrosion resistance [14].

The conductivity value of Pt-Ru/C electrodes is 6.61×10^{-4} S/cm. Electrical conductivity is obtained based on the solution resistance value and charge transfer resistance obtained from fitting results based on the formula in equation 1:

$$\sigma = \frac{1}{Z_R} \times \frac{l}{A} \dots\dots\dots(1)$$

where: $Z_R = R_p + R_s$; R_s is a prisoner of the charge solution of transfer resistance [11, 12].

Testing the MEA Performance at DAFC

Open Circuit Voltage (OCV) Testing

MEA performance testing begins with the measurement of OCV measured using the Won2tech SMART2 Fuel Cell Test System. The value of OCV owned by MEA is 0.650 V. This value is the initial voltage that is owned before being given a load. The greater the OCV value indicates that the number of active catalyst sites is large. However, the value of OCV is not enough to determine MEA performance in general so that performance testing is based on what can be described in the I-V and I-P performance curves.

MEA Performance Testing based on the I-V and I-P Performance Curve

Performance testing is carried out by giving varying currents on each MEA with the same concentration, namely methanol and ethanol 2 M. Methanol and ethanol are very influential in electrochemical reactions especially at the anode side due to contact

between fuel and electrodes. however, cross over can occur which causes a decrease in a performance marked by the appearance of heat on the stack DAFC [17]. MEA performance testing based on the I-V performance curve (polarization curve) can be seen in Figure 4.

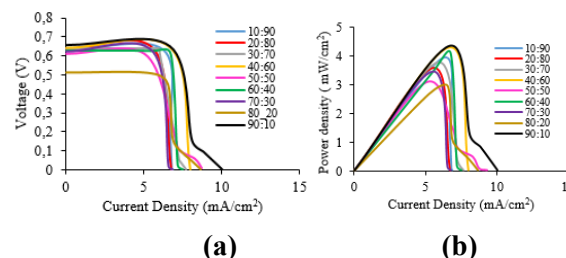


Figure 4. Curves of (a) I-V and (b) I-P performance of MEA DAFC in the ratio of methanol and ethanol vary

Figure 4 shows the relationship between voltage to current density and between the power density to current density. The greater the current density, the greater the density of power produced. This is because power is the product of voltage and current density.

Based on MEA performance testing based on I-V and I-P performance curves, the best ratio of methanol and ethanol volume is 90:10. This determination is based on the ability to maintain voltage and power when there is an increase in current density with a maximum power density of 4.34 mW/cm² and is able to maintain the voltage at 0.649 V under conditions of 6.875 mA/cm². The size of MEA ability to maintain voltage and power is also influenced by competitive adsorption that occurs between methanol and ethanol.

CONCLUSION

The catalytic activity of electrodes affects the performance of the MEA. The large ECSA value and electrical conductivity indicate good electrode performance. Meanwhile, the performance of MEA is clarified by measuring the value of OCV and testing performance under loading conditions. Comparison of the mixture volume of methanol and ethanol 2 M has a difference to the performance obtained in accordance with the ability of MEA as a place of competition for adsorption between methanol and ethanol.

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