Utilization of catalyst-coated membrane (CCM) and spraying methods in fabrication membrane electrode assembly (MEA) for direct methanol fuel Cell (DMFC) using Pt-Co / C catalyst

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Abstract. Utilization of Catalyst-Coated Membrane (CCM) and Spraying Methods in fabrication of Membrane Electrode Assembly (MEA) for Direct Methanol Fuel Cell (DMFC) using a varied Pt-Co/C catalyst has been carried out. The use of Pt-Co/C catalyst is intended to reduce the use of Pt catalysts in the electrode. Electrodes and MEAs of the two methods are characterized and tested for performance, both in open circuit voltage (OCV) and under load conditions. The MEA performance test results with the spraying method show that the best performance MEA is obtained at the ratio of Pt:Co = 60:40, while with the CCM method, the best MEA is obtained at the ratio of Pt:Co = 40:60. However, the power density of the spraying method in the best conditions is greater than the CCM method.

1. Introduction
Direct Methanol Fuel Cell (DMFC) is one type of fuel cell with methanol as its fuel. DMFC is projected to meet the needs of portable power, such as those developed by Toshiba, Hitachi, Fujitsu and Samsung [1]. Fabrication DMFC electrodes is generally carried out by casting methods [2]. The obstacle of the casting method is the difficulty to control the level of thickness and porosity of the electrode. Another method often used in fabrication electrode is the spraying method [3] and the Catalyst Coated Membrane (CCM) methods [4]. The spraying method and the CCM method are widely used in making electrodes for PEMFC. In this study, electrodes and MEA were made using the spraying method and the CCM method for DMFC [5].

The most important component in DMFC (as is the case with PEMFC) is the Membrane Electrode Assembly (MEA) which is the center of the electrochemical reaction for the conversion of methanol (fuel) and oxygen (oxidants) into electricity and water as waste. MEA is a combination of cathode and anode that flank the electrolyte membrane on both sides[6]. Because the important function, the MEA must get special attention in terms of efforts to achieve high current density and durability. The thing that needs to be studied to produce high-performance MEA is the content and type of catalyst in the electrode and the method of making it.

Making DMFC electrodes is generally carried out by casting method [2]. The obstacle of the casting method is the difficulty in controlling the level of thickness and porosity of the electrode. In addition, the casting method will be difficult if the catalyst layer consists of several layers. Another method that is often used in making electrodes is the spraying method[7] and the Catalyst Coated Membrane (CCM) methods [8]. The last two methods are widely used in making electrodes for PEMFC. In this study compared both spraying methods and the CCM method in making electrodes and MEA for DMFC.
2. Experimental Section

2.1. Making of Gas Diffusion Layer (GDL) [9]
Making of GDL is done by attaching MPL (Microporous Layer) ink which consists of a mixture of carbon vulcan-XC72, PTFE and Ammonium bicarbonate using the spraying methods onto Backing layer (BL).

2.2. Making of Catalyst Layer (CL)
The Catalyst layer was made by mixing Pt-Co / C catalyst with various concentration with 2-propanol as solvent and nafion solution, then mixed in an ultrasonic homogenizer.

2.3. Making of Electrode and MEA
The electrodes are made in two ways, namely the spraying method by spraying the catalyst layer for the cathode and the anode onto the GDL then glued to both sides of the nafion-117 membrane to make the MEA. The second method is the CCM method where the catalyst layer is sprayed onto both sides of the membrane then GDL is attached to both sides of the membrane. The electrodes produced are characterized using XRD and Electrochemical Impedance Spectroscopy (EIS) and electrical conductivity analysis. MEA is made by pressing heat at a 135°C at a pressure of 2000 psi for 3 minutes.

3. Results and Discussion

3.1. XRD Analysis
XRD analysis of electrodes can be seen in Figure 1 below.

![Figure 1. Diffractogram of electrode containing Pt/C, Pt-Co/C and Co/C catalyst.](image)

Based on the XRD measurement results shown in Figure 1, the three electrodes (with Pt/C, Pt-Co/C and Co/C catalysts) show the diffraction pattern of the elements. This can be seen from the location and shape of the peak diffractogram for the element. A high peak at position 2θ = 22-29° shows the presence of carbon, while the peak in position 2θ = 40-45° shows the presence of platinum (JCPDS No.01-1194). However, the cobalt peak is not detected specifically, this is because the substituted cobalt is in the form of amorph so that XRD cannot detect it specifically. Cobalt peaks are usually seen at 20 = 45° and 65° (10).

3.2. EIS Analysis
Electrochemical characterization and performance tests of the electrode, especially in the CL, are accomplished in various ways, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS). EIS is quite widely used by researchers for characterizing and testing PEMFC. EIS can be operated without damage, providing detailed diagnostic information on electrochemical phenomena included in the load transfer reactions at the electrode and electrolyte interface, the reaction mechanism and the electrode material properties.

The Analysis EIS of electrodes with various Pt-Co/C catalyst composition were described in figure 2.

![EIS Spectra of the electrodes with various composition of Pt-Co/C Catalyst](image)

**Figure 2.** EIS Spectra of the electrodes with various composition of Pt-Co/C Catalyst

One of the performance of electrodes can be seen from the small impedance. Based on Figure 2 it can be seen that the electrode with the composition Pt:Co = 20:80 has a small impedance, as does Pt:Co = 0:100. This shows the opportunity to use cobalt as a companion catalyst for fuel cell electrodes.

### 3.3. Electrical Conductivity Analysis

Measuring the conductivity of Pt-Co/C electrodes is done to see the ability of the electrodes to deliver electric current. Conductivity analysis is one of the supporting parameters for determining the quality of an electrode. The electrical conductivity analysis results from the spraying method and the CCM method are presented in Figures 3.

![Electrical Conductivity of electrode](image)

**Figure 3.** Electrical Conductivity of electrode (a) CCM Methods (b) spraying methods
Based on Figure 3, the electrical conductivity of Pt:Co = 20:80 and 40:60 have the highest conductivity, so it have the opportunity to be used as electrode for the fuel cell.

3.4. MEA Performances
The MEA performance test is carried out to see the profile of the effect of current density on voltage and power density at various current densities. MEA performance of the two methods are shown in Figures 4 and 5.

![Figure 4](image1.png)

**Figure 4.** MEA Performance of electrode with the CCM Methods (a) I-V (b) P-I Performance

![Figure 5](image2.png)

**Figure 5.** MEA Performance of electrode with the spraying methods (a) I-V (b) P-I performance

Based on Figure 4, it can be seen that MEA with Pt:Co catalyst content = 40:60 made with the CCM method has the best performance, while in Figure 5, MEA with Pt:Co catalyst content = 60:40 made by spraying method is the best performance. The factor that determines the performance of MEA is the high open circuit voltage (OCV) and the ability of MEA to maintain voltage at an increasing current density. In addition, in general, the performance of MEA will increase with increasing catalyst content, until the optimum active surface area of the catalyst is reached. The results of MEA performance measurements indicate that cobalt can be used as a supporting catalyst for platinum.

4. Conclusions
Based on the results of EIS analysis and electrical conductivity, electrodes with Pt-Co content = 20:80 and 40:60 show good performance. Meanwhile, the results of performance tests on the MEA with the spraying method found that the best performance was obtained at the ratio of Pt:Co = 60:40 and with the CCM method at the ratio of Pt:Co = 40:60, but the spraying method produced better performance.

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