Preparation and Characterization of Ti-Co/C catalyst for PEMFC Cathode

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Abstract

Operational cost issues have been concern in Proton Exchange Membrane Fuel Cell (PEMFC). Especially on cathode electrodes that using platinum as its catalyst. Platinum is expensive and it can lead to electrolyte poisoning, Non-platinum Group Metal (Non-PGM) catalysts was chosen to overcome those problems above. A Ti-Co/C catalyst was prepared using impregnation-reduction method and characterized using cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) methods. This study aimed to compare the result between matrix carbon Vulcan XC-72R and Dots carbon which was applied to Ti-Co/C catalyst, also to compare the method of coating catalyst on GDL layer were Doctor Blade and spraying methods. The result was confirmed that Ti-Co/C with the ratio of Ti:Co 50:50, using Dots carbon as its matrix and spraying method preparation has ECSA value and conductivity respectively 28.72 cm^2/g and 0.16 x 10^{-3} S/cm, those were the highest value than another method. The conclusion of this study was non-platinum catalyst Ti-Co/C which used Dots carbon as a matrix and the spraying method showed a good response as a cathode catalyst of PEMFC.

Keywords: PEMFC, Catalyst, Dots, Vulcan, Impregnation-Reduction, Cathode, and Ti-Co/C

Abstrak (Indonesian)

Biaya operasional telah menjadi pusat perhatian dalam penelitian *Proton Exchange Membrane Fuel Cell* (PEMFC). Khususnya pada elektroda katoda yang menggunakan platina sebagai katalisnya karena harganya yang mahal. Katalis dari golongan non-platina (Non-PGM) dikembangkan untuk mengatasi hal tersebut. Katalis Ti-Co/C telah dibuat menggunakan metode impregnasi-reduksi dan dikarakterisasi menggunakan metode *Cyclic Voltametry* (CV) dan *Electrochemical Impedance Spectroscopy* (EIS). Penelitian ini bertujuan untuk membandingkan hasil antara katalis Ti-Co/C yang menggunakan matriks karbon Vulcan XC-72 dengan karbon Dots, serta membandingkan metode pelapisan katalis ke GDL dengan alat Doctor Blade dan metode penyemprotan (*spraying*). Katalis Ti-Co/C dengan perbandingan Ti:Co 50:50, menggunakan matriks karbon Dots dan metode *spraying* memiliki nilai ECSA dan konduktifitas berturut-turut sebesar 28,72 cm^2/g dan 0,1688 x 10^{-3} S/cm. Nilai ini merupakan hasil tertinggi dibandingkan dengan metode lainnya. Kesimpulan dari penelitian ini adalah katalis non-platina Ti-Co/C dengan menggunakan matriks karbon Dots dan metode penyemprotan menunjukkan respon yang baik sebagai katalis katoda PEMFC.

Kata Kunci: Katalis, Karbon Dots, Karbon Vulcan, Impregnasi-Reduksi, Katoda, dan Ti-Co/C

INTRODUCTION

Proton Exchange Membrane Fuel Cell (PEMFC) has become one of the technologies to be developed by researchers to solve fossil energy problems and current environmental issues. Many points of view make PEMFC one of the superior energy sources of the

future, they are energy-producing technology that is free of CO_2 gas emissions, modular, has a high energy density when its compared to conventional energy sources [1], high efficiency, time short start-up, and low operating temperature [2].

Theoretically, PEMFC can produce a voltage up to 1.2 Volts when it's operating in open-circuit voltage with a low operating temperature below 100 ºC [3-4]. When viewed from the application point of view, PEMFC can be applied to all fields with low-temperature operations such as mobile technology, vehicles, and also as an emergency energy provider [5-6].

The issues of cost and durability are the main problems of PEMFC. Membrane Electrode Assembly (MEA) and Pt electrocatalyst spend the cost about 40% - 50% of the total price of PEMFC [7-8], while based on data from the United States Department of Energy (DoE), platinum spend the cost about 56% of the total cost for PEMFC assembly [9].

Even though Pt is the best catalyst for PEMFC, but the cost issue has broken the fuel cell application efficiency. Therefore, many researchers study about Non-platinum Group Metal (Non-PGM) catalysts recently, even the results were not good as using Pt [10–14]. In this study, transition metal titanium was combined with cobalt to get the best performer as the catalyst. Titanium is a corrosion-resistant and inert metal, one of the studies about titanium as a catalyst of PEMFC has been done by Yin (2014), the study was preparation Ti-Co-Phen/C using polymer complex synthesis method, and the result it has a power density of about 0.68 W/cm^2 with excellent performance stability [14].

Impregnation-reduction was used as a synthesis method, it is a simple method to load porous support with a certain volume of solution or metal component (containing the precursor of the active phase) is contacted with the solid (support) in the solid-state [15-16], whereby hydrogen gas was used as a reducing agent.

In this study, there were several types of matrix materials (support) used. They were carbon Vulcan XC-72R and Dots carbon matrix (CDs). Carbon Vulcan XC-72R is often used for PEMFC applications. Due to the emergence of difficult environmental challenges, carbon-based materials, particularly CDs, have sparked a lot of attention in the disciplines of energy conversion and storage [17]. CDs are one of the newest carbon materials and have good electron transfer capabilities, so they can increase the catalyst activity in the ORR reaction [9]. The functional groups on the surface of CDs (-OH, -COOH, -NH$_2$, etc.) can be used as active coordination sites for transition metal ions.

Several factors that affect the performance of the catalyst, include dispersed finely over the supporting material. Coating methods include the Doctor Blade method and spraying method were usually used. Spray coating is a method that involves forcing a coating substance through a nozzle to create a fine aerosol. To improve the direction and quality of aerosol spray deposition, the method can be combined with a carrier gas and electrostatic charge. The Doctor Blade method involves depositing the solution in front of the blade and moving the blade across the surface in line with the surface to create a wet film. This procedure should have solution losses of under 5% in theory, but finding optimal circumstances takes time in practice [18].

MATERIALS AND METHODS
Materials
The materials that were used in this study are $TiCl_3$ (Merck-Germany), $CoCl_2.6H_2O$ (Univar), NH_3 Solution 25% (Merck-Germany). Carbon Vulcan XC-72R (Fuel Cell Store) and Dots carbon were used as the matrix in the form of Ti-Co/C. Other materials that are used are 2-propanol (Sigma-Aldrich), Nafion NR 212 solution (Fuel Cell Store), PTFE emulsion DISP 30LX (Fuel Cell Store), isopropyl alcohol, and ammonium bicarbonate (Merck).

Methods
The catalyst was prepared by using the impregnation-reduction method. The catalyst in this study was a combination of titanium and cobalt catalyst in carbon Vulcan XC-72R or dots carbon matrix to be formed as Ti-Co/C, the weight ratio of each composition was 50:50 for each comparison of Ti and Co, so that each metals in the catalyst did not show a dominant reaction to the others. The surface of electrode was identified using digital microscope.

Catalyst Ti-Co/C Preparation
The titanium trichloride 1.17 mol/L was pipetted approximately 0.7 mL, $CoCl_2·6H_2O$ as much as 0.1782 grams, matrix carbon 0,1838 grams, and distilled water (until paste formed) were mixed well using a magnetic stirrer for 24 hours, at the first 4 hours, the solution was dripped drop by drop using NH_3 solution. After 24 hours, the pH of the solution was neutralized. Furthermore, the mixture was calcined using a furnace at 550 ºC for 5 hours, then reduced using a horizontal furnace with H_2 gas flowing at 450 ºC for 2 hours, but previously the horizontal furnace was cleaned of first from O_2 gas using N_2 gas [19]. Based on Yin & Li

experiment [14], the loading of the catalyst was 3.5 mg/cm^2 with an electrode surface area was 25 cm^2.

Gas Diffusion Layer (GDL) Preparation

GDL was prepared by measuring carbon Vulcan XC-72R 0.0825 grams was dissolved by isopropyl alcohol 2 mL, and then added with ammonium bicarbonate 0.04125 grams little by little. Next, the mixture was stirred using a magnetic stirrer for 700 rpm and 60 minutes, while the mixture was added by 30 wt% of PTFE. Then finished by stirring at 700 rpm for 30 minutes. In the last step, the mixture was sprayed on the carbon paper using a spray gun and calcined in furnace at 350 ºC for 3 hours. The step above was used for every 25 cm^2 of the electrode.

PEMFC Cathode Electrode Preparation Using Spraying Method

The previously prepared catalyst was taken about 0.3128 grams, then added by Nafion NR 212 solution 0.2659 grams, and dissolved by 2-propanol. The mixture was stirred for about 60 minutes, furthermore added by 30 wt% of PTFE, stirring was resumed until 30 minutes. The mixture was sprayed using spray gun tools on the GDL with a surface area of 25 cm^2 that have been prepared before. At the last step, the electrode was sintered in the furnace at 350ºC for about 3 hours.

PEMFC Cathode Electrode Preparation Using Doctor Blade Method

The catalyst 0,3128 grams, Nafion NR 212 solution 0.2659 grams, and 30 wt% of PTFE were dissolved using 2-propanol, the mixture was stirred for 30 minutes until the paste formed. The mixture was dropped on the top of the GDL 25 cm^2 layer, then Doctor Blade machine rolled on the top of GDL that contains the catalyst mixture with a speed of 70 mm/s. Finally, the electrode was dried at 80 ºC for 30 minutes, and sintered in the furnace at 350 ºC for about 3 hours.

Data Analysis

The catalyst that has been prepared was characterized using cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The CV and EIS analysis were performed using Autolab PGSTAT 302N and data processing was done by NOVA software version 1.8.14. The analysis was used Pt electrode plat as a counter electrode, Ag/AgCl electrode as a reference electrode, and synthesized electrode as a working electrode.

The catalytic activity of the Ti-Co/C catalyst was determined by calculating the electrochemical surface area (ECSA) [20] shown in equation (1) :

$$\mathrm{E}CSA = \frac{QH}{(Lc \times prop.consant)} \quad (1)$$

Where ECSA is electrochemical surface area (cm^2/g), QH is a charge based on the area under the hydrogen desorption peak (mC/cm^2), Lc was catalyst loading, and proportionally constant of metal that was used in the study.

The electrical conductivity was measured by:

$$\sigma = \frac{1}{Zr} \times \frac{l}{A} \quad (2)$$

Where σ was conductivity (S/cm), Zr was a total resistance counted by Rp + Rs (Ω), l was a pallet thickness (cm), and A was an electrode contact surface area (cm^2).

RESULTS AND DISCUSSION

Cathode catalyst for PEMFC Ti-Co/C has been prepared by using the impregnation-reduction method. The result of the experiment using the same matrix carbon and different coating the catalyst on the GDL layer method was spraying had better dispersion based on digital microscopy captured. That was identified by the surface appearance of the electrode, Fig. 1.a had even surface than the Fig. 1.b.
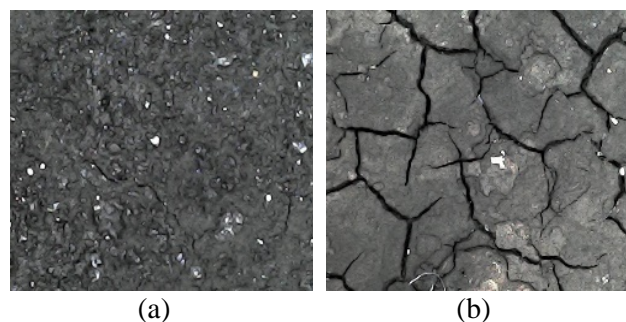

       (a)   (b)

Figure 1. Microscopy Capture Using Digital Microscope (a) Ti-Co/Vulcan 50:50 Spraying Method and (b) Ti-Co/Vulcan 50:50 Doctor Blade Method

It can be seen from the surface appearance (Fig. 1), whereby the catalyst which was coated using spraying method showed a negligible cracking, so it was better surface than using Doctor Blade that appeared the high cracking surface. A cracking surface can reduce the electrochemical activity of the catalyst because of the dispersion of catalyst on the GDL was uneven, so it can reduce the electrical contact in the MEAs, causes the cell performance decrease [21].

Figure 2. Microscopy Capture Using Digital Microscope of Ti-Co/Dots 50:50 Spraying Method Surface

Furthermore, the research was continued by using the spraying method and then comparing the carbon matrix Vulcan carbon and Dots carbon (Fig. 2). The results obtained were the distribution of the catalyst on the surface of the GDL was quite good, there was no cracked surface. Then the active surface area of the results was measured using CV and EIS analysis.

CV Analysis

CV analysis has been done by NOVA software version 1.8.14 to see the catalytic activity of the catalyst that has been prepared. The CV analysis results are shown in Figure. 3.
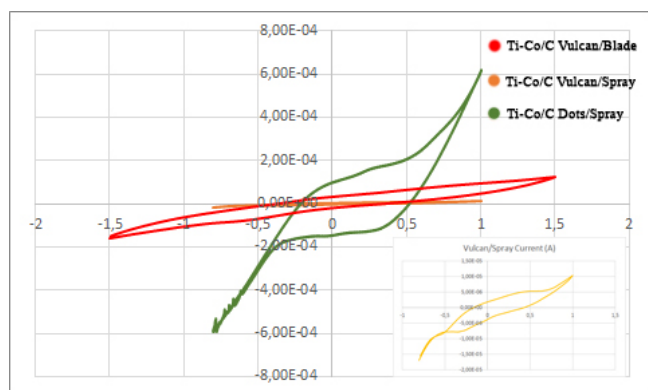

Figure 3. The CV curve for Ti-Co/C in various of methods and matrix carbon

Based on Fig. 3 it was figured that the only catalyst showing the reversible catalytic activity was Ti:Co ratio 50:50 with Dots carbon matrix and spraying method (green peak). This indicates that titanium and cobalt were distributed and also have more active sites

scattered on the Dots carbon matrix. It was also shown from ECSA calculations that Ti-Co/C with Dots carbon and spraying method has the highest ECSA value (the ECSA values of various Ti-Co/C were measured refers to Eq. 1 and presented in Table. 1). The highest ECSA indicated the quantitative active site of catalyst particles, so it means the catalyst have the highest conductivity. Conductivity is the electrical property of the metal to be able to conduct the electricity. ECSA is not linear with conductivity sometimes, because it depends on conducting electrical ability of the metal.

A good matrix is the one that can disperse the catalyst evenly, if the catalyst was dispersed well, it will accelerate the chemical reaction because of the active site increased, so it produces the high ECSA value.

Table 1. ECSA data of Ti-Co/C catalyst for various of method and matrix carbon

Catalyst	ECSA (cm^2/g)
Ti-Co/C Vulcan/Spraying	2.3426
Ti-Co/C Vulcan/Dr Blade	2.0454
Ti-Co/C Dots/Spraying	28.7210

Table.1 presents the Ti-Co/C catalyst with Dots carbon matrix and the spraying preparation method has the highest ECSA numbers. This was relatable with surface appearance (microscopy capture) on the same data above.

EIS Analysis

EIS was used to determine standard characterization techniques for many applications, such as fuel cell, batteries, corrosion, etc. The data during EIS analysis was collected as diagrammatic representation, Nyquist plot consisting one or more semi-circular region which indicate the activities at the anode and cathode. In this study, the obtained curves were fitted to a mathematical model, which represented as a kind of electrical circuit (equivalent circuit) in order to get the impedance value.

Based on Table. 1 showed that the Ti-Co/C with Dots carbon and spraying preparation method had the smaller impedance plots. Electrical impedance is a measure of the electrical resistance at an alternating current (AC) source, so that the smaller impedance plots indicated the higher of conductivity and catalyst activity. The data was showed on Fig. 4 and Fig. 5.
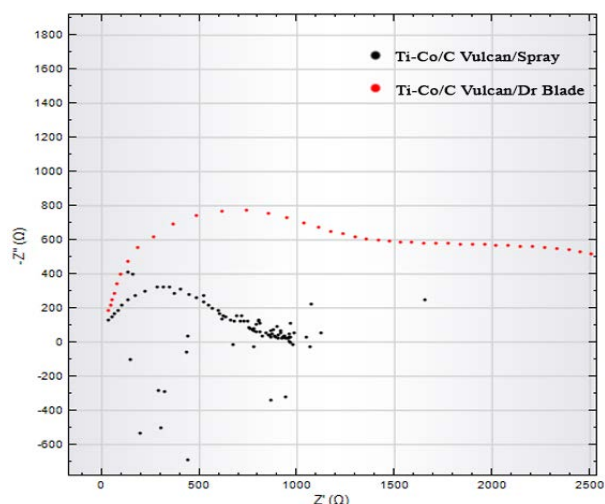
Figure 4. The EIS spectra of Ti-Co/C in coating method comparison (Spray and Doctor Blade) with the same matrix carbon
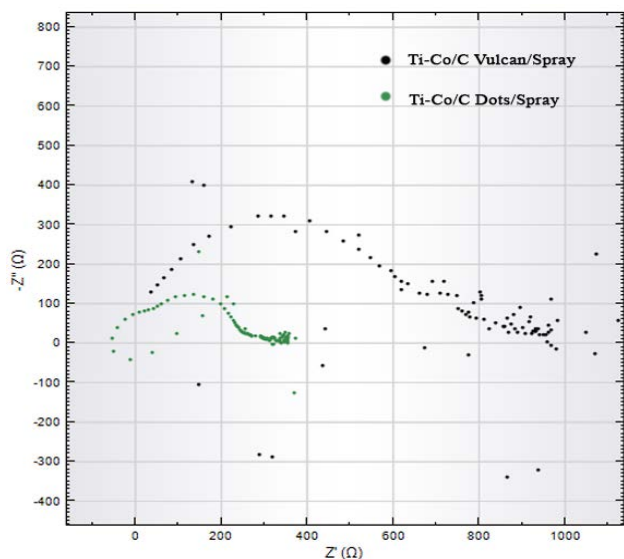

Figure 5. The EIS spectra of Ti-Co/C in matrix comparison (Dots dan Vulcan) with the same coating method

The Ti-Co were impregnated in CDs may enhance the electrocatalytic performance by promoting the transfer of electrons by internal interactions and can be an efficient electrocatalyst for ORR [22].

The Nyquist plot that was obtained by EIS analysist than was calculated the conductivity by Eq. 2. Table 2 described the result of conductivity calculations, it showed the highest conductivity was owned by Ti-Co/Dots with spraying preparation, with the number of conductivity was 0.16 S/cm, which was twice times from using Vulcan matrix means that Ti-Co/Dots Spraying method more conductive than other sample in this study.

Table 2. Conductivity data of Ti-Co/C catalyst for various of method and matrix carbon

Catalyst	Conductivity (S/cm)
Ti-Co/C Vulcan/Spraying	0.06
Ti-Co/C Vulcan/Dr Blade	0.02
Ti-Co/C Dots/Spraying	0.16

The preparation by spraying allowed for low cracking, therefore an even surface was obtained. Using Dots carbon as a matrix might increase the catalyst activity in the ORR reaction, because of containing functional group (-OH, -COOH, -NH$_2$, etc.) on the CDs [9].

CONCLUSION

The impregnation-reduction catalyst Ti-Co/C ratio of Ti:Co 50:50 with various coating method and matrix carbon have been done well. The result based on the CV and EIS analysis was Ti-Co/C with matrix Dots carbon and spraying method showed the highest value. The Dots carbon matrix used with spraying method can increase the active site of the catalyst, so it increases the conductivity values.

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