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Fabrication and Characterization of Pt-Co/C Catalyst for Fuel Cell Electrode

Dedi Rohendi¹, Addy Rachmat¹, Nirwan Syarif¹

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Jl. Palembang-Prabumulih Km. 32 Inderalaya Ogan Ilir, South Sumatera, Indonesia

Email: rohendi19@gmail.com / rohendi19@unsri.ac.id

Abstract. One of the most important components in fuel cell is electrode which hold as center for electrochemical reaction on converting fuel and oxygen into electricity. Special attention hence must be given to this component in order to achieve high performance especially on its catalytic activity and durability. To obtain such performance, some aspect must be take into consideration i.e. the content and type of catalyst as well as preparation method. Impregnation-reduction and electrodeposition method were evaluated on fabrication of fuel cell electrode from Pt-Co/C catalyst using $H_2PtCl_6 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ in carbon Vulcan XC-72 substrate. Transition metal other than platinum as supporting catalyst was used not only to enhance catalytic activity but also to reduced cost and avoid poisoning which platinum suffers easily. Characterization of catalyst using Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) confirmed that catalyst made from Pt-Co/C using ratio Pt : Co = 20:80 has good catalytic activity for fuel cell application. XRD diffractogram showed result of Pt reduction at $2\text{-theta} = 39.76^\circ$ (111) and 46.23° (200) while the present of Co is not clear at $2\text{-theta} = 44.51^\circ$ and 51.85° . Co was not detected due to it became an alloy with Pt and relatively small concentration (20%). Pt-Co/C catalyst prepared by impregnation-reduction and electrodeposition methods can be used as catalyst support in fuel cell electrode.

Keywords; Pt-Co/C; catalyst layer, fuel cell electrode.

1. Introduction

Fuel cell is an electrochemical equipment that can convert free energy available in fuel (chemical energy) directly into useful work in the form of electrical energy [1, 2]. Fuel cells with advantages on high conversion rates, low pollution levels, modular and diverse fuel sources are expected to replace existing conventional energy sources [3, 4]. Fuel Cells technology will surely be present in Indonesia due to the growing pressure to bring clean energy sources. Currently, the application of fuel cells in the world has entered to the commercialization stage for vehicles, while in Indonesia, fuel cell has started to be used as a source of backup power in Base Transceiver Station (BTS) without the support of independence in the mastery of technology.

Two type of fuel cell with the advantage of low operating temperatures, high conversion rates and diverse applications (portable equipment, vehicles and stationary energy sources) is the Proton Exchange Membrane Fuel Cell (PEMFC) and Direct Methanol Fuel Cell (DMFC)[1, 5].

One of the most important components in PEMFC/DMFC are the electrode contained in Membrane Electrode Assembly (MEA). Electrodes are the center of the electrochemical reaction of converting hydrogen and oxygen gas into electrical energy and water as effluents [6, 7]. Because the very important function, the PEMFC/DMFC electrode must get special attention in the effort of achieving high performance, especially in its catalytic activity and its durability [2]. MEA with high current density can significantly reduce PEMFC/DMFC stack size and decrease Pt catalyst content will decrease overall fuel cell price.



The catalysts used in fuel cell electrodes are generally platinum-based catalysts that are quite expensive and are easily poisoned [8-10]. In addition to a platinum single catalyst, using of other transition metal groups other than platinum is reportedly used as a platinum support catalyst [11-13]. It is intended to improve the catalytic function of the electrode and reduce the platinum content [10]. In this research, we used the alloys of Pt catalyst with Co in the carbon vulcan XC-72 as a substrate.

The aim of this research is to make and characterize Pt-Co / C catalyst for use in PEMFC electrode. The use of Pt catalyst alloys with Co is intended to reduce the use of Pt in the electrode and improve the catalytic function of the catalyst. The process of preparing of the catalyst is carried out by the reduction method based on a previous study [14].

2. Experimental Section

Material & Instrumentation

The material used in this study are $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich). Electrodes are made from backing layer (Avcarb P75T), microporous layer and catalyst layer. The catalyst prepared in this study was a combination of platinum and cobalt catalysts in the XC-72 vulcanized carbon matrix in the form of Pt-Co / C by weight ratio of each composition 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100 for comparison of Pt to Co. The CV and EIS analysis were performed using Autolab PGSTAT 302N and data processing was done with NOVA software version 1.8.14. The analysis was performed by using Pt electrode as counter electrode, Ag / AgCl / KCl electrode as reference electrode and electrode produced as working electrode with scan rate 50 mV / sec. Analysis of CV using electrolyte solution of H_2SO_4 0,3 M.

Procedure

Preparation of Pt-Co/C catalyst for spraying method was carried out by the method of impregnation and reduction of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution simultaneously on a vulcanized carbon powder matrix XC-72 with 1 M NaBH_4 solution as reducing agent. The resulting catalyst is then used to prepare the electrode with the spraying methods. The resulting catalyst was characterized using cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and X-Ray diffraction (XRD) analysis. The catalytic activity of the catalyst is determined by calculating the electrochemical surface area (ECSA).

3. Results and Discussion

CV Analysis

CV analysis was performed to see the catalytic activity of the catalyst prepared. The CV analysis results are shown in Figure 1.

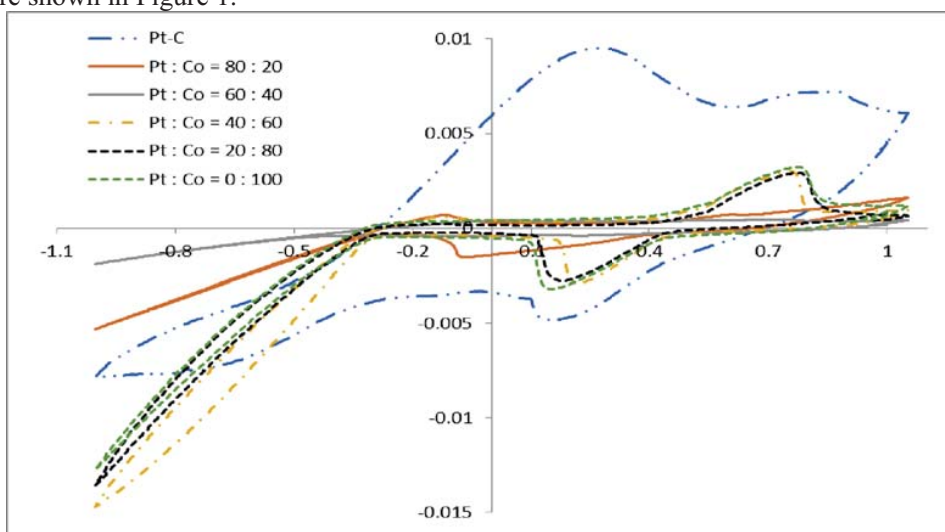


Figure 1. The CV curve for alloys of Pt / C and Pt-Co/C catalysts in various compositions

Based on Fig. 1 it can be seen that there are catalytic activity in almost all Pt-Co/C catalyst compositions, especially starting from Pt:Co = 40:60 composition showing reversible catalytic activity. In the catalyst composition Pt: Co = 0: 100, cathodic and anodic peaks are almost same like to the composition of 40:60 and 20:80. This indicates the expectation using Co catalyst as a support for Pt catalyst. Pt/C Catalyst have biggest area but not reversible. It can also be seen from ECSA calculations in which Pt / C catalyst has the highest ECSA value.

The ECSA values for each of the Pt-Co / C catalyst compositions are presented in Table 1.

Table 1. ECSA data for Pt / C and Pt-Co / C catalysts on various compositions

Catalyst	ECSA (m ² /g)
Pt/C 100 : 0	37,381
Pt-Co/C 80 : 20	18,700
Pt-Co/C 60 : 40	16,433
Pt-Co/C 40 : 60	17,285
Pt-Co/C 20 : 80	17,640
Pt-Co/C 0 : 100	25,284

The Pt/C catalyst (table 1) has the highest ECSA values. This is understandable because Pt is the main catalyst that used in PEMFC to convert hydrogen and oxygen gas into water. However, the catalytic activity of Co as a support of Pt catalyst is quite dominant, even in the Pt-Co/C 0:100 composition having a fairly high ECSA. This suggests that Co is a fairly responsive catalyst in catalyzing the reaction.

XRD Analysis

XRD observations for Pt-Co/C catalysts are shown in Fig. 2 and the combined results of all observations are shown in FIG. 3.

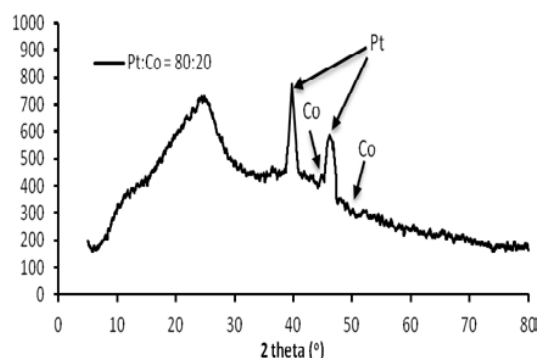


Figure 2. XRD pattern for Pt-Co/C catalyst (Pt:Co = 80:20)

Figure 2 shows the appearance of peak Pt at $2\theta = 39.76^\circ$ (111) and 46.23° (200) [14]. Co's presence is not so obvious at $2\theta = 44.51^\circ$ and 51.85° . This is because Co particles are part of alloys with Pt with a relatively small concentration (20% b/b). The same results are also shown in previous studies [12, 14]. Meanwhile, the peak distribution between $2\theta = 19$ to 26° shows a typical peak for carbon. The higher of the Co content, the peak Co becomes more visible. This can be seen from Figure 3.

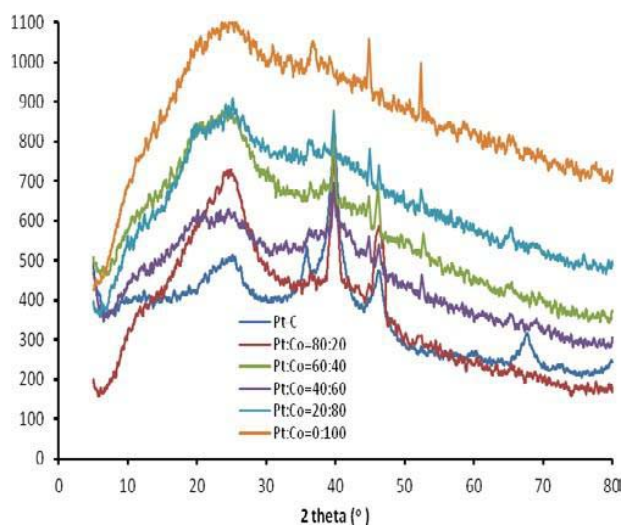


Figure 3. XRD pattern for combined Pt/C and Pt-Co/C catalysts in various compositions

Electrochemical Impedance Spectroscopy (EIS) Analysis

EIS is a perturbative characterization of the dynamics of an electrochemical process. EIS is widely used as a standard characterization technique for many material systems and applications (corrosion, plating, batteries, fuel cells, etc.). The EIS measurement data is shown in Figure 4.

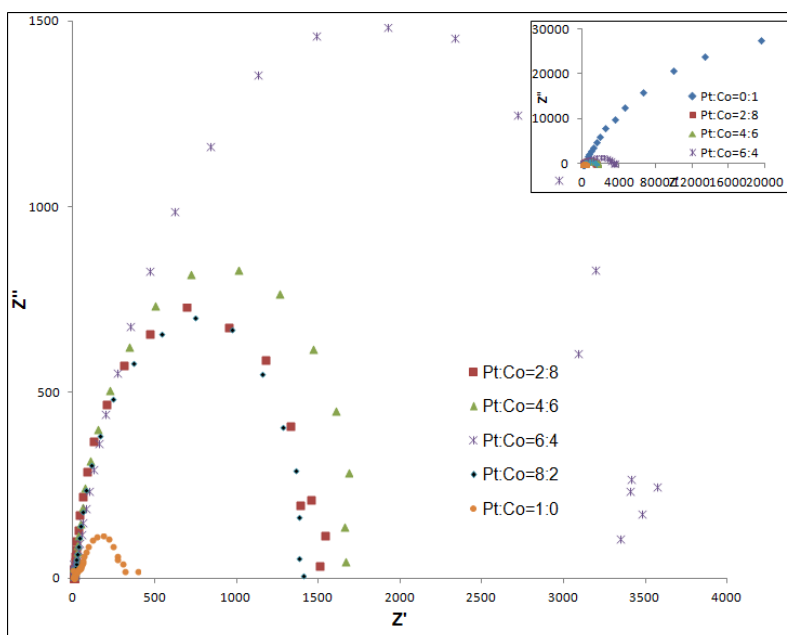


Figure 4. EIS spektra for Pt-Co/C catalyst alloys

Figure 4 shows the EIS curve of the Pt-Co/C catalyst. Based on the EIS results, the higher of the Pt level, the smaller the impedance that indicating the higher of the conductivity and catalyst activity. Although the performance of Co acting as a single catalyst (Pt: Co = 0: 1) looks good by CV and ECSA analysis, the EIS measurements show very large impedances (inset images). Thus, the alloying composition of Pt catalyst with the lowest Co that can be used is Pt: Co = 20:80.

Conclusion

The reduction process of $\text{H}_2\text{PtC}_6 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the carbon matrix by using NaBH_4 as the reducing agent successfully formed Pt-Co/C catalyst and alloy Pt and Co with composition Pt:Co = 20:80, showed good catalytic activity, as indicated by CV and EIS analysis.

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