

Article

Characterization of Electrode with Cu₂O-ZnO/C and Pt-Ru/C Catalyst for Electrochemical Reduction CO₂ to CH₃OH

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Abstract

Electrode characterization has been carried out with Cu₂O-ZnO/C and Pt-Ru/C catalysts to convert carbon dioxide to methanol. Characterization are carried out with XRD analysis, Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The electrodes are made by distributing Cu₂O-ZnO/C and/or Pt-Ru/C catalyst by spraying method. The results of XRD analysis showed that the characteristic peak of platinum was $2\theta = 39.7 - 40.74^{\circ}$ with an intensity of 970 cps and 1384 cps and the diffraction peak of Ru oxide was found at 47.02° with an intensity of 923 cps. The peak of Cu₂O characteristics appeared at 36.12° with an intensity of 88 cps and the peak for ZnO characteristics at 68.2° with an intensity of 13 cps. The test results with the cyclic voltammetry method showed that the electrode with a Cu₂O-ZnO/C catalyst obtained the highest ECSA value which was 26.044 cm²/g, with an electrical conductivity value of 3.4 x 10⁻³ S/cm and a total real resistance of 5.9425 Ω .

Keywords: ECSA, MEA, carbon dioxide, Pt-Ru/C, Cu₂O-ZnO/C

Abstrak (Indonesian)

Telah dilakukan karakterisasi elektroda dengan katalis Cu₂O-ZnO/C dan Pt-Ru/C untuk konversi karbon dioksida menjadi metanol. Karakterisasi yang dilakukan meliputi analisis XRD, *Cyclic Voltammetry* (CV) dan *Electrochemical Impedance Spectroscopy* (EIS). Elektroda dibuat dengan mendistribusikan katalis Cu₂O-ZnO/C dan/atau Pt-Ru/C dengan metode penyemprotan. Hasil analisis XRD menunjukkan puncak karakteristik platina pada $2\theta = 39.7^{\circ} - 40.74^{\circ}$ dengan intensitas 970 cps dan 1384 cps dan puncak difraksi Ru oksida ditemukan pada 47.02° dengan intensitas 923 cps. Puncak karakteristik Cu₂O muncul pada 36.12° dengan intensitas 88 cps dan puncak karakteristik ZnO pada 68.2° dengan intensitas 13 cps. Hasil pengujian dengan metode CV menunjukkan bahwa elektroda dengan katalis Cu₂O-ZnO/C menghasilkan nilai ECSA paling tinggi yaitu sebesar 26.044 cm²/g dengan nilai konduktivitas listrik sebesar 3.4 x 10⁻³ S/cm dan hambatan real total 5.9425 Ω.

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Kata Kunci: ECSA, MEA, karbon dioksida, Pt-Ru/C, Cu₂O-ZnO/C

INTRODUCTION

The increasing concentration of CO_2 in the atmosphere due to industrial activities and vehicle emissions causes various health and environmental issues[1]. Therefore, it is required to utilize CO_2 to reduce the impact, one of them is by converting CO_2 into valuable chemicals. In addition, it can also provide

a double solution, namely reducing the amount of CO₂ in the atmosphere and producing valuable compounds.

CO₂ conversion can be done by several methods, namely thermochemistry [2], photochemistry [3], photo-electrochemistry [4], biochemistry [5], and electrochemistry [6]. One of the most potential products from the synthesis of CO₂-based compounds is methanol [7], [6]. So far methanol has been widely used as an additive in the internal combustion engine (ICE) and as a fuel for Direct Methanol Fuel Cell (DMFC) [8].

Methanol is produced on an industrial scale through hydrogenation reactions, but requires high pressure and temperature [9]. The electrochemical reduction method can be carried out at ambient temperatures and can use water as a proton source [10]. Electrochemical reduction can be done with liquid electrolytes such as KHCO3 [6, 8-10] and solid polymer electrode (SPE) [5, 7, 11-14]. One of the factors that influence electrochemical reduction is the catalyst selection, therefore a catalyst that has a high catalytic activity and has selectivity towards methanol formation is required. Copper-based catalysts have been widely used in the electrochemical reduction of CO₂ to methanol [6-9, 13, 14], other metal catalysts have also been widely studied in recent years, including platinum catalysts as noble metals [5, 7, 13, 15]. Generally, electrochemical reduction is mostly carried out on bulk electrodes in electrolyte solutions, but it was found that limitations on mass transport and low solubility of CO₂ in electrolytes. Gas Diffusion Electrode (GDE) are considered to be able to overcome deficiencies in the use of bulk electrode because they can reduce the mass transport limit [10], [15].

This study used Pt-Ru/C and Cu₂O-ZnO/C catalysts at the cathode and Pt/C catalysts at the anode. Electrodes were characterized using X-Ray Diffraction (XRD), Cyclic Voltammetry (CV) and, Electrochemical Impedance Spectroscopy (EIS) to test the performance of the electrodes.

MATERIALS AND METHODS Materials

Electrolyzers Cell, Mass Flow Controller, Spray Gun, Furnace, hydraulic hot press, Ultrasonic homogenizer, analytical balance, glassware, potensiostat AUTOLAB PGSTAT204 Metrohm, X-Ray Diffractometer Rigaku MiniFlex 600, power supply, HEM-Shaker,

Carbon paper Avcarb P75T (FuelCell store), carbon vulcan XC-72R (FuelCell store), Polytetrafluoroethylene (PTFE) (FuelCell store), membrane Nafion-117 (FuelCell store), Nafion solution (FuelCell store), 2-propanol (Mercks), Pt/C (40%) (FuelCell store), Cu₂O (99,99%, Sigma Aldrich), ZnO (99,99%, Sigma Aldrich), NaOH (Mercks), H₂O₂ (Mercks) and H₂SO₄ (Mercks).

Methods

The electrodes consisted of a cathode and anode with a size of 7 x 7 cm with a catalyst loading of 2 mg.cm⁻² on each electrode. Electrode preparation is

made by mixing Pt-Ru/C and/or Cu₂O-ZnO/C powder with a small amount of deionized water until homogeny and stirring using a spatula. Next, the nafion solution and 2-propanol were added to the catalyst mixture, then the mixture was agitated for 10 minutes in an ultrasonic homogenizer. The mixture is added with PTFE and stirring is continued for 5 minutes until it forms a paste. The paste is sprayed onto carbon paper, then sintered at 350 °C for 3 hours.

RESULTS AND DISCUSSION *Electrode Characterization using XRD*

XRD characterization was used to identify the crystal structure and determine the crystal size of the catalyst used. Samples were measured at a scan speed of 10 deg / min and scan range of $5^{\circ} \le 2\theta \le 80^{\circ}$. The diffractogram of Pt/C, Cu₂O-ZnO/C and Pt-Ru/C can be seen in Figure 1.



Figure 1. Diffractogram of (a) Pt/C (b) Pt-Ru/C and (c) Cu₂O-ZnO/C

Figure 1 shows a diffractogram of the electrodes used, with a peak at $2\theta \sim 26^{\circ}$ characteristic of the carbon vulcan XC-72R (carbon support). XRD data showed crystalline peaks at 2θ indicating the presence of metal particles in the sample. Some of the peaks show similarities to the JCPDS reference. In Figure 1 (a) shows the diffractogram of Pt/C, the diffraction peak is obtained at a value of $2\theta = 39.7^{\circ}$ with an intensity of 970 cps which indicates the presence of Pt crystals with a face centered cubic (fcc) shape based on JCPDS 04-0802 [18]. The diffractogram of Pt-Ru/C can be seen in Figure 1 (b), obtained a peak that widened at $2\theta = 40.74$ ° with an intensity of 1384 cps, and 68.8° with an intensity of 179 cps which indicates the presence of Pt, the diffraction peak on the catalyst. Pt-Ru is slightly shifted to a higher 2θ value when compared to the Pt/C diffractogram, this proves the formation of the alloy from Pt-Ru in the catalyst, whereas at $2\theta = 47.02^{\circ}$ with an intensity of 923 cps. It

is considered a peak of Ru, but the observations are not clear, and the absence of peaks associated with the hexagonal closed packed (hcp) structure typical of pure Ru. So that the possibility of Ru forming an alloy with Pt atom as an oxide in amorphous form (based on JCPDS 21-1172) [17, 18]. These data are compared with previous studies conducted by Kashyout [18] and Chetty [17] which obtained a peak of Ru at $2\theta = 44^{\circ}$.

Figure 1 (c) shows the diffractogram of Cu₂O-ZnO/C, the diffraction peaks are obtained at a value of $2\theta = 36.12^{\circ}$ with an intensity of 88 cps which indicates the cubic phase of Cu₂O based on JCPDS 75-1531 [21] and at a value of $2\theta = 68.2^{\circ}$ with an intensity of 13 cps is a ZnO hexagonal phase based on JCPDS 36-1451 [20] [21]. Whereas the peak at $2\theta \sim 12^{\circ}-20^{\circ}$ which tends to widen is the result of amorphous $(2\theta \sim 16^\circ)$ and $(2\theta \sim 18^\circ)$ scattering crystal of the nafion perfluorocarbon chain. The peaks at $2\theta \sim 18^{\circ}$ which tend to be higher and sharper are considered to be the plane (100) of the PTFE crystals [24], while the lower and wider peaks indicate the content of the nation. The summary of XRD measurement results can be seen in Table 1.

Table 1. Crystal Size of Different Electrode

No.	Electrode	Identification	2θ (deg)	D (nm)
1.	Pt/C	Pt	39.7	1.296
2.	Pt-Ru/C	Pt Ru	40.74 47.02	2.701 1.220
3.	Cu ₂ O-ZnO/C	Cu ₂ O ZnO	36.12 68.2	18.1 7.542

The digital XRD data obtained can be used to calculate the crystal size using the Debye-Scherrer equation as in equation 1. Based on the results of the calculations carried out, the crystal size for each electrode was obtained, as shown in Table 1. Based on Table 1, it can be seen that the Pt/C electrode has the smallest crystal size of 1.296 nm.

Electrode Testing using the Cyclic Voltammetry (CV) Method

This test was carried out to obtain the Electrochemical Surface Area (ECSA) value which measure of represents а the number of electrochemically active sites per gram of catalyst [25], and to determine the reactivity of the electrodes by observed at the reduction and oxidation (redox) reactions of the sample. The voltammogram consists of 2 peaks, namely the oxidation peak in the positive current region and the reduction peak in the negative current region [26]. In cyclic voltammetry the current response is measured as a function of potential, the

application of potential is carried out back and forth so that the reduction and oxidation processes can be observed properly. The measurement results are shown in Figure 2.



Figure 2. Voltammogram of different electrode with scan rate 50 mV/s

The results of the calculation of the ECSA value for each sample are shown in Table 2. Based on the results of ECSA calculations, it was found that the electrode with a Pt/C catalyst produced an ECSA value of 121.076 cm²/g, an electrode with a Pt-Ru/C catalyst had an ECSA value of 12.484 cm²/g and a Cu₂O-ZnO/C of 26.044 cm²/g.

Table 2. ECSA of Electrode with Different Catalyst

No.	Katalis	ECSA (cm ² /g)
1.	Pt/C	121.076
2.	Pt-Ru/C	12.484
3.	Cu ₂ O-ZnO/C	26.044

The highest ECSA value was obtained at the electrode with Pt/C catalyst. This shows that the distribution of Pt/C catalyst on the electrode surface is more even than that of Pt-Ru/C and Cu₂O-ZnO/C. Therefore, Pt/C catalyst is used at the anode side because the water oxidation process requires a higher catalytic activity. One of the factors that can increase the dispersion of the catalyst is the size of the catalyst particles. The smaller crystal size has the potential to produce a high ECSA value, and vice versa [18]. However, the small crystal size does not necessarily result in a high ECSA value if the distribution is uneven. In this study, the electrode with a Pt-Ru/C catalyst had a smaller particle size than Cu₂O-ZnO, but had a smaller ECSA value than Cu₂O. The causative factor that may occur is the occurrence of agglomeration in the catalyst paste, so that the distribution of the catalyst is not optimal.

A high ECSA value indicates that the active site on the electrode surface is present in large numbers, thus allowing optimal electrochemical reactions to occur [27]. The ECSA value also describes the effective charge-transfer resistance at the electrode, where the greater the ECSA value, the smaller the resistance. Effective charge transfer resistance affects the ability of MEA to deliver protons [28].

Testing of Electrochemical Impedance Spectroscopy (EIS) and Electrical Conductivity

The Electrochemical Impedance Spectroscopy (EIS) method is a method that can be used to measure the electronic conductivity of electrode sheets [29]. EIS is used to determine the movement of electrons and ionics, the movement of the phase angle at the electrodes. This method can show the separation between ionic and electron conductivity from a resulting graph [30].

Based on the results of the EIS measurements taken, the Nyquist curve is obtained as shown in Figure 3. The Pt/C electrode with a catalyst loading of 2 mg/cm² has a total real resistance value (Z_R) of 5.8409 Ω , Pt-Ru/C 2 mg/cm² of 9.6416 Ω , and Cu₂O-ZnO/C of 5.9425 Ω . The Z_R value is obtained from the results of the fitting in the form of extrapolation that forms a semicircle as in Figure 3; from the Z_R value, conductivity can be determined using equation 3. Figure 3 shows that the Pt/C and Cu₂O-ZnO/C electrodes has a low resistance value and means high conductivity, while the electrode with a Pt-Ru/C catalyst has a higher resistance value.



Figure 3. Nyquist Curves from Different Electrodes

The conductivity values for each sample are shown in Table 3. Based on Table 3, it can be seen that the Cu₂O-ZnO/C catalyst has a higher conductivity value than the Pt-Ru/C catalyst, this can be caused by the even distribution of the catalyst particles which increases the conductivity value [29]. The low electrical conductivity value on the electrode with Pt-Ru/C catalyst can be caused by the agglomeration in the catalyst paste, agglomeration can reduce the conductivity at the cathode so that the capacity is low [31]. Electrodes that have a high electrical conductivity value allow the accessibility of the specimen to react and support efficient product release [32].

Table 3.	Electrical	Conductivity	from	Different
	Electrodes			

Electrodes						
	Impedance		edance	Electrical		
No.	Sampel	Parameter		Conductivity		
		$\operatorname{Rp}(\Omega)$	$\operatorname{Rs}(\Omega)$	(S/cm)		
1.	Pt/C	5.8092	0.0317	3.5 x 10 ⁻³		
2.	Pt-Ru/C	6.8831	2.7585	2.1 x 10 ⁻³		
3.	Cu ₂ O-	6.3649	-0.4224	3.4 x 10 ⁻³		
	ZnO/C					

CONCLUSION

The results of electrode characterization using XRD obtained the characteristics peaks of platinum at 39.7° and 40.74°, 47.02° (Ru oxide), 36.12° (Cu₂O), and at $2\theta = 68.2^{\circ}$ (ZnO). The results of the CV analysis of the electrode with Cu₂O-ZnO/C catalyst obtained the highest ECSA value of 26.044 cm²/g correlated with the results of the EIS analysis which resulted in an electrical conductivity of 3.4 x 10⁻³ S/cm.

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