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 2θ = 39.7 – 40.74° with an intensity of 970 cps and 1384 cps and the diffraction peak of Ru oxide was found at 47.02⁰ with an intensity of 923 cps. The peak of Cu2O characteristics appeared at 36.12⁰ with an intensity of 88 cps and the peak for ZnO characteristics at 68.2⁰ 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, CO2, Pt-Ru/C, Cu2O-ZnO/C

INTRODUCTION
The increasing concentration of CO2 in the atmosphere due to industrial activities and vehicle emissions causes various health and environmental issues[1]. Therefore, it is required to utilize CO2 to reduce the impact, one of them is by converting CO2 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 produced.
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 electrolyte (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, potensioskat 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° ≤ 2θ ≤ 80°. The diffracogram of Pt/C, Cu2O-ZnO/C and Pt-Ru/C can be seen in Figure 1.

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

Figure 1 shows a diffracogram of the electrodes used, with a peak at 2θ ~ 26° 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 2θ = 39.7° 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 2θ = 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 2θ = 47.02° 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 2θ = 44°.

Figure 1 (c) shows the diffractogram of Cu2O-ZnO/C, the diffraction peaks are obtained at a value of 2θ = 36.12° with an intensity of 88 cps which indicates the cubic phase of Cu2O based on JCPDS 75-1531 [21] and at a value of 2θ = 68.2° with an intensity of 13 cps is a ZnO hexagonal phase based on JCPDS 36-1451 [20] [21]. Whereas the peak at 2θ ~ 12°-20° which tends to widen is the result of amorphous (2θ~16°) and crystal (2θ~18°) scattering of the nafion perfluorocarbon chain. The peaks at 2θ ~ 18° 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 nafion. 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                     | 39.7     | 1.296 |
| 2.  | Pt-Ru/C                  | 40.74    | 2.701 |
| 3.  | Cu2O-ZnO/C               | 36.12    | 18.1  |

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 represents a measure of 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.

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 (cm²/g) |
|-----|---------------|--------------|
| 1.  | Pt/C          | 121.076      |
| 2.  | Pt-Ru/C       | 12.484       |
| 3.  | Cu2O-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.

**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 2θ = 68.2° (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 $3.4 \times 10^{-3}$ S/cm.

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**REFERENCES**

[1] H. P. Yang, Y. N. Yue, S. Qin, H. Wang, and J. X. Lu, “Selective electrochemical reduction of CO₂ to different alcohol products by an organically doped alloy catalyst,” *Green Chem.*, vol. 18, no. 11, pp. 3216–3220, 2016, doi: 10.1039/c6gc00091f.

[2] K. Atsonios, K. D. Panopoulos, and E. Kakaras, “Thermocatalytic CO₂ hydrogenation for methanol and ethanol production: Process improvements,” *Int. J. Hydrogen Energy*, pp. 1–15, 2015, doi: 10.1016/j.ijhydene.2015.12.001.

[3] G. Zeng, J. Qiu, Z. Li, P. Pavaskar, and S. B. Cronin, “CO₂ reduction to methanol on TiO₂-passivated GaP photocatalysts,” *ACS Catalysis*, vol. 4, no. 10, pp. 3512–3516, 2014, doi: 10.1021/cs500697w.

[4] E. E. Barton, D. M. Rampulla, and A. B. Bocarsly, “Selective solar-driven reduction of
CO₂ to methanol using a catalyzed p-GaP based photoelectrochemical cell,” *J. Am. Chem. Soc.*, vol. 130, no. 20, pp. 6342–6344, 2008, doi: 10.1021/ja0776327.

[5] S. Schlager, L. M. Dumitru, M. Haberbauer, A. Fuchsblauer, H. Neugebauer, D. Hiemetsberger, A. Wagner, E. Portenkircher, and N. S. Sariciftci, “Electrochemical Reduction of Carbon Dioxide to Methanol by Direct Injection of Electrons into Immobilized Enzymes on a Modified Electrode,” *ChemSusChem*, vol. 9, no. 6, pp. 631–635, 2016, doi: 10.1002/cssc.201501496.

[6] K. P. Kuhl, T. Hatsukade, E. R. Cave, D. N. Abram, J. Kibsgaard, and T. F. Jaramillo, “Electrocatalytic Conversion of Carbon Dioxide to Methane and Methanol on Transition Metal Surfaces,” *J. Am. Chem. Soc.*, vol. 136, no. 40, pp. 14107–14113, 2014, doi: 10.1021/ja505791r.

[7] C. Jones, E. Robertson, V. Arora, P. Friedlingstein, E. Shevliakova, L. Bopp, V. Brovkin, T. Hajima, E. Kato, M. Kawamiya, S. Liddicoat, K. Lindsay, C. H. Reick, and T. Hajima, “Twenty-first-century compatible CO₂ emissions and airborne fraction simulated by CMIP5 earth system models under four representative concentration pathways,” *J. Clim.*, vol. 26, no. 13, pp. 4398–4413, 2013, doi: 10.1175/JCLI-D-12-00554.1.

[8] S. Shironita, K. Karasuda, K. Sato, and M. Umeda, “Methanol generation by CO₂ reduction at a Pt-Ru/C electrocatalyst using a membrane electrode assembly,” *J. Power Sources*, vol. 240, pp. 404–410, 2013, doi: 10.1016/j.jpowsour.2013.04.034.

[9] M. Le, M. Ren, Z. Zhang, P. T. Sprunger, R. L. Kurtz, and J. C. Flake, “Electrochemical Reduction of CO₂ to CH₃OH at Copper Oxide Surfaces,” vol. 158, no. 5, pp. 45–49, 2011, doi: 10.1149/1.3561636.

[10] L. M. Aeshala, R. G. Uppaluri, and A. Verma, “Effect of cationic and anionic solid polymer electrolyte on direct electrochemical reduction of gaseous CO₂ to fuel,” *J. CO₂ Util.*, vol. 3–4, pp. 49–55, 2013, doi: 10.1016/j.jcou.2013.09.004.

[11] J. Albo, G. Beobide, P. Castaño, and A. Irabien, “Methanol electrosynthesis from CO₂ at Cu₂O/ZnO prompted by pyridine-based aqueous solutions,” *J. CO₂ Util.*, vol. 18, pp. 164–172, 2017, doi: 10.1016/j.jcou.2017.02.003.

[12] J. Hazarika and M. S. Manna, “Electrochemical reduction of CO₂ to methanol with synthesized Cu₂O nanocatalyst: Study of the selectivity,” *Electrochim. Acta*, vol. 328, p. 135053, 2019, doi: 10.1016/j.electacta.2019.135053.

[13] J. Albo and A. Irabien, “Cu₂O-loaded gas diffusion electrodes for the continuous electrochemical reduction of CO₂ to methanol,” *J. Catal.*, vol. 2015, doi: 10.1016/j.jcat.2015.11.014.

[14] R. Venka, “Design and Development of Electrochemical Cell for Converting Carbon Dioxide to Useful Fuel,” Arizona State University, 2016.

[15] M. Sassenburg, “Conducting CO₂ reduction at a bipolar membrane electrode assembly,” 2018.

[16] D. Yang, Q. Zhu, C. Chen, H. Liu, Z. Liu, Z. Zhao, X. Zhang, S. Liu, and B. Han, “Selective electroreduction of carbon dioxide to methanol on copper selenide nanocatalysts,” *Nat. Commun.*, vol. 10, no. 1, pp. 1–9, 2019, doi: 10.1038/s41467-019-08653-9.

[17] N. Gutiérrez-Guerra, L. Moreno-López, J. C. Serrano-Ruiz, J. L. Valverde, and A. de Lucas-Consuegra, “Gas phase electrocatalytic conversion of CO₂ to syn-fuels on Cu based catalysts-electrodes,” *Appl. Catal. B Environ.*, vol. 188, pp. 272–282, 2016, doi: 10.1016/j.apcatb.2016.02.010.

[18] H. A. Huy, T. Van Man, H. T. Tai, and H. T. T. Van, “Preparation and characterization of high-dispersed Pt/C nano-electrocatalysts for fuel cell applications,” *J. Sci. Technol.*, vol. 54, no. 4, 2016, doi: 10.15625/0866-708x/54/4/7308.

[19] R. Chetty, W. Xia, S. Kundu, M. Bron, T. Reinecke, W. Schuhmann, and M. Muhler, “Effect of reduction temperature on the preparation and characterization of Pt-Ru nanoparticles on multiwalled carbon nanotubes,” *Langmuir*, vol. 25, no. 6, pp. 3853–3860, 2009, doi: 10.1021/la804039w.

[20] A. B. Kashyout, A. B. A. Nasser, L. Giorgi, T. Maiyalagan, and B. A. B. Youssef, “Electrooxidation of methanol on carbon supported Pt-Ru nanocatalysts prepared by ethanol reduction method,” *Int. J. Electrochem. Sci.*, vol. 6, no. 2, pp. 379–393, 2011.

[21] S. K. Baek, K. R. Lee, and H. K. Cho, “Oxide p-n heterojunction of Cu₂O/ZnO nanowires and their photovoltaic performance,” *J. Nanomater.*, vol. 2013, 2013, doi: 10.1155/2013/421371.
[22] I. Sakellis, S. Giamini, I. Moschos, C. Chandrinou, A. Travlos, C.Y. Kim, J. J. Lee, J. G. Kim, and N. Boukos, “A novel method for the growth of Cu2O/ZnO heterojunctions,” *Energy Procedia*, vol. 60, no. C, pp. 37–42, 2014, doi: 10.1016/j.egypro.2014.12.339.

[23] H. Liu, Z. Hu, R. Hu, B. Liu, H. Ruan, L. Zhang, and W. Xiao, “Large-scale synthesis of Cu2O nanocubes and their electrochemical properties,” *Int. J. Electrochem. Sci.*, vol. 11, no. 4, pp. 2756–2761, 2016, doi: 10.20964/110402756.

[24] X. Teng, C. Sun, J. Dai, H. Liu, J. Su, and F. Li, “Solution casting Nafion/polytetrafluoroethylene membrane for vanadium redox flow battery application,” *Electrochim. Acta*, vol. 88, pp. 725–734, 2013, doi: 10.1016/j.electacta.2012.10.093.

[25] C. Jackson, “Preparation and Characterisation of Pt-Ru/C Catalysts for Direct Methanol Fuel Cells,” University of Cape Town, 2014.

[26] T. Lestaringgisih, Q. Sabina, and N. Majid, “Penambahan TiO2 dalam Pembuatan Lembaran Polimer Elektrolit Berpengaruh Terhadap Konduktivitas dan Kinerja Baterai Lithium,” *J. Mater. dan Energi Indones.*, vol. 7, no. 1, pp. 31–37, 2017.

[27] D. A. Stevens and J. R. Dahn, “Electrochemical Characterization of the Active Surface in Carbon-Supported Platinum Electro catalysts for PEM Fuel Cells,” *J. Electrochem. Soc.*, vol. 150, no. 6, p. A770, 2003, doi: 10.1149/1.1573195.

[28] B. Pranoto, V. J. Wargadalam, H. A. Al-Rasyid, “Catalyst Coating On Fuel Cell Of MEA Fabrication Process Type PEM,” vol. 12, no. 1, pp. 21–34, 2013.

[29] L. romaida Samosir, “Analisis Sifat Elektrokimia dan Karakteristik Pvd-Hfp/Libob dan PvdF-Hfp/Litfsi sebagai Elektrolit Padat pada Baterai Litium Coin Cell,” Universitas Sumatera Utara, 2019.

[30] M. Dzulqornain, “Sintesis Composite Polymer Electrolyte dari Polyvinylidene Fluoride-Hexafluoropropylene (PVDF-HFP) dan Lithium Carbonate (Li2CO3) Untuk Baterai Lithium,” Institut Pertanian Bogor, 2018.

[31] S. Achmad, E. Suwandi, Ramlan, and T. H. Utama, “Efek Penambahan Bahan Aditif MWCNT Dan Acetylene,” *Univ. Sriwij.*, vol. 16, no. 2, pp. 49–54, 2015.

[32] A. J. Martin, G. O. Larrazabal, and J. Perez-Ramirez, “Towards sustainable fuels and chemicals through the electrochemical reduction of CO2: Lessons from water electrolysis,” *Green Chem.*, vol. 17, no. 12, pp. 5114–5130, 2015, doi: 10.1039/c5ge01893e.