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Synthesis of AuPt Bimetal and its Catalytic Properties in Ethanol Electrooxidation Reaction

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Abstract

AuPt Bimetal has been successfully synthesized by electrodeposition method with potentiostat technique. By varying the concentration of Au ions in the solution they are able to control the morphology and composition of the synthesized sample. The morphology obtained from the AuPt synthesis is cauliflower. The effect of Au ion concentration in solution on the catalytic performance of AuPt, the greater the Au concentration, the greater the current density in the electrooxidation reaction. In addition, the concentration of Au ions in the solution affects the results of the deposition of Au and Pt elements. In the study of AuPt nanocatalysts with a 0.4 mM Au ion concentration in an electrolyte solution, it was shown to have good catalytic activity in the ethanol electrooxidation reaction, with the resulting current densities and I_f/I_b of 10.1 mA/cm^2 and 43.53 mA/cm^2, respectively. This is an implication of many Au compositions which are known to have the ability to absorb and oxidize CO to encourage an increase in current density and increase its catalytic activity.

Keywords: AuPt, electrodeposition, electrooxidation ethanol.

1. Introduction

Direct Alcohol Fuel Cells (DAFC) are one of the most promising and attention-grabbing chemical resources due to their high energy conversion efficiency, carried out at room temperature, and the formation of no or few pollutants [1]. Commonly used alcohols include methanol, ethanol, and ethylene glycol [2–4]. Of the various alcohols, ethanol is an attractive fuel material because it can be produced in large quantities from biomass and is less toxic than methanol and ethylene glycol. In addition, ethanol has a higher energy density when completely oxidized to CO_2 because it releases 12 electrons per molecule [5].

One of the good materials used as a catalyst in ethanol electro-oxidation is bimetallic nanoparticles. In previous studies, Pt-based bimetallic catalysts were widely used because they have good catalytic properties in oxidation-reduction reactions, for example, PtBi and PtPd for ethylene glycol electro-oxidation reaction, PtRh, and PtSn for ethanol electro-oxidation [4-7]. AuPt bimetallic nanocatalyst has the highest current for methanol electro-oxidation reaction compared to other bimetals [8]. In methanol electrooxidation, AuPt has the longest lifetime compared to other bimetals which is 90 days [9]. Bimetallic AuPt has been studied in methanol electro-oxidation reactions, AuPt produces higher catalytic activity compared to monometallic Au and Pt. Therefore, the addition of Au is expected to minimize CO poisoning on Pt electrodes because Au nanoparticles show good catalytic activity in the CO to CO_2 oxidation reaction. In addition, Au also has a higher electronegativity value than Pt so it encourages an increase in charge transfer from Pt to Au which causes the Pt d-orbitals to be empty and can be used for electro-oxidation reactions [10].

AuPt nanoparticles (AuPt NPs) have been synthesized by several methods, including liquid-phase deposition, one-pot wet-chemical, and electrodeposition methods [9-12]. The reactivity of a nanocatalyst can be determined from the fineness of its size and shape. The resulting size and shape depend on the synthesis process. AuPt synthesis has been carried out with different morphologies including AuPt nanowires, and AuPt nanocauliflower [11,13]. Therefore, a synthesis method that can control the morphology and composition.

of the catalyst is needed to improve the catalytic activity for the ethanol electro-oxidation reaction.

Therefore, this study aims to synthesize AuPt bimetallic nanoparticles on fluorine-doped tin oxide (FTO) substrate using the electrodeposition method. In this study, the electrodeposition method was used because of its low difficulty, does not require a lot of chemicals, low temperature, produces finer nanoparticles, and can easily regulate the growth of nanocrystal nuclei [7]. The synthesis of AuPt is varied in Au concentration because the concentration of Au ions affects the catalytic properties of AuPt bimetals. The catalytic properties of AuPt bimetals were tested in 0.1 M NaOH and 1 M ethanol using Cyclic Voltammetry (CV).

2. Materials and Method

2.1 Synthesize of AuPt NPs

AuPt NPs were synthesized by the electrodeposition method of the potentiostat technique in a three-electrode system. Before electrodeposition, a multimeter was prepared to measure the voltage of the FTO-glass substrate and determine the conductive side of the substrate to be coated by the deposit. Then the substrate was washed using technical ethanol and distilled water slowly until the dirt on the substrate disappeared. Then the substrate was allowed to dry.

Electrolyte solutions were made as much as 25 mL for each of the three electrodeposition times having the following composition: K_2PtCl_6 1mM + $HAuCl_4$ x mM (x = 0.1 mM; 0.2 mM; and 0.4 mM) in sulfuric acid (H_2SO_4). The prepared electrolyte was then put into an electrodeposition cell which contained a Pt electrode as a counter electrode, Ag/AgCl is the reference electrode, and FTO glass (3 x 10 mm) as the working electrode. Then the three electrodes were inserted into the electrodeposition cell. Then electrodeposition was carried out with a voltage of -300 mV and a time of 300 s.

2.2 Characterization

The characterization performed is SEM-EDX (Scanning Electron Microscopy - Energy Dispersive X-ray) used to characterize the morphology and composition of AuPt NPs.

2.3 Electrochemical test

EIS analysis was used to determine the electron transfer resistance (R_{ct}) of AuPt. EIS analysis was measured at a frequency of 50kHz - 0.1Hz in 0.5M KCl solution. CV analysis was performed to determine the catalytic activity of the AuPt NPs in 0.1 M NaOH and 1 M ethanol solutions. The potential used is between -750 mV to 750 mV, scan rate of 25 mV/s, starting from the anodic current.

3. Results and Discussion

The AuPt electrodeposition process occurs in reduction and oxidation reactions, where reduction occurs at the working electrode and oxidation occurs at the counter electrode.

Reactions that occur at the working electrode [14]:

$$AuCl_4- + 3e^- \rightarrow Au_{(s)} + 4Cl^- \quad (1)$$

$$PtCl_6^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^- \quad (2)$$

$$PtCl_4^{2-} + 2e^- \rightarrow Pt_{(s)} + 4Cl^- \quad (3)$$

Reaction that occurs at the counter electrode:

$$2H_2O \rightarrow 4H^+ + O_2 + 2e^- \quad (4)$$

SEM analysis was conducted to determine the effect of varying Au ion concentrations on the morphology of AuPt. Figure 1 shows the measurement results of AuPt samples by SEM synthesized under the following conditions: -300 mV voltage for 300 s at room temperature, and varying $HAuCl_4$ concentrations of 0.1 mM, 0.2 mM, and 0.4 mM.

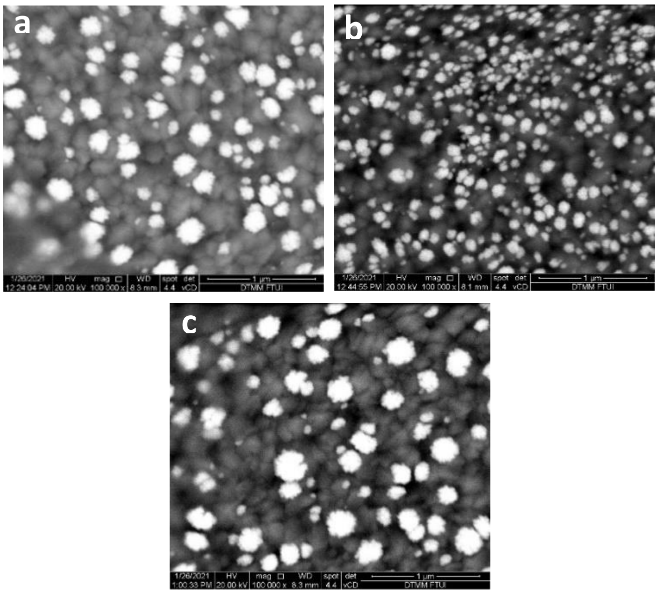

Figure 1. SEM of AuPt with varying concentrations of Au ions a) 0.1 mM, b) 0.2 mM, c) 0.4 mM, at 100,000x magnification.

Figure 1 shows the morphology of AuPt surfaces grown on the FTO-glass substrate at 100,000 x SEM magnification. It can be seen that in AuPt with low Au concentration ($HAuCl_4$ 0.1 mM), the resulting shape is more like Pt where there are sharp protrusions because the Pt element is more dominant than Au (Fig. 1a). In AuPt with 0.2 mM $HAuCl_4$ concentration, the resulting shape is more dense and tight (Fig. 1b). In AuPt with $HAuCl_4$ concentration, the cauliflower shape is produced (Fig. 1c).

Analysis with EDX instrument to determine the effect of Au ion concentration on AuPt composition. EDX results on AuPt samples with fixed K_2PtCl_6 concentration (1mM) and several variations of Au ions (0.1 mM, 0.2 mM, 0.4 mM) can be seen in Fig. 2.

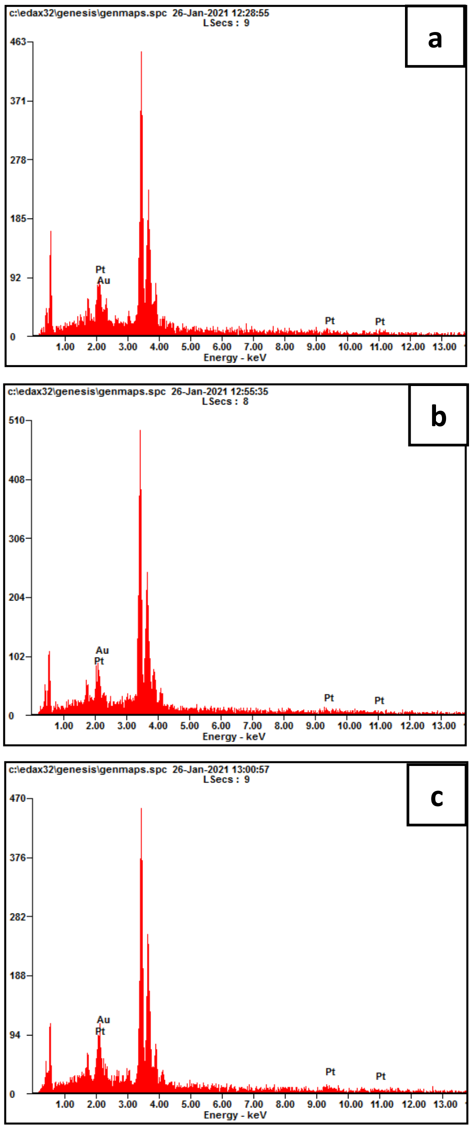

Figure 2. EDX results of AuPt NPs with varying concentrations of $HAuCl_4$ a) 0.1 mM, b) 0.2 mM, c) 0.4 mM, with a fixed concentration of K_2PtCl_6 1mM.

In the EDX results, the AuPt sample containing 0.1 mM Au ion concentration has an elemental composition of Au and Pt of 13.48% and 86.52%, respectively. The AuPt sample containing 0.2 mM Au ion concentration has an elemental composition of Au and Pt of 21.38% and 78.62%, respectively. The AuPt sample containing 0.4 mM Au ion concentration has an elemental composition of Au and Pt of 39.23% and 60.76%, respectively. Figure 3. shows a graph of the elemental composition of Au and Pt in AuPt samples.

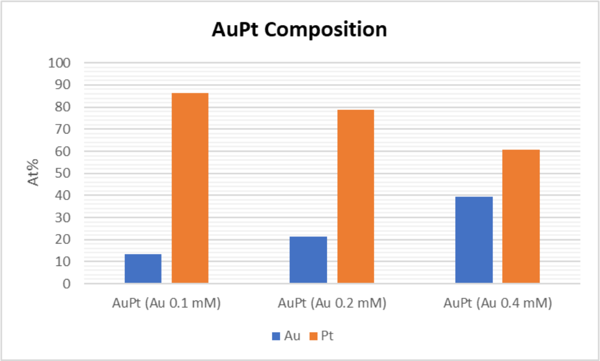

Figure 3. Composition chart of AuPt sample.

From the EDX results shown in Figure 3 it is found that the more the concentration of Au ions increases, the more Au elements will be deposited. The measured Au content increases and Pt content decreases with the increase in Au^{3+} addition. In all three samples, the dominant element is Pt because the concentration of Pt ions is more than Au ions.

Electrochemical Impedance Spectroscopy (EIS) analysis is used to determine the R_{ct}. Where the semicircle in the Nyquist plot at high frequency is characteristic of the electron transfer process, and the diameter of the semicircle is equal to the electron transfer resistance [15]. Figure 4 shows the Nyquist plot of the AuPt sample.

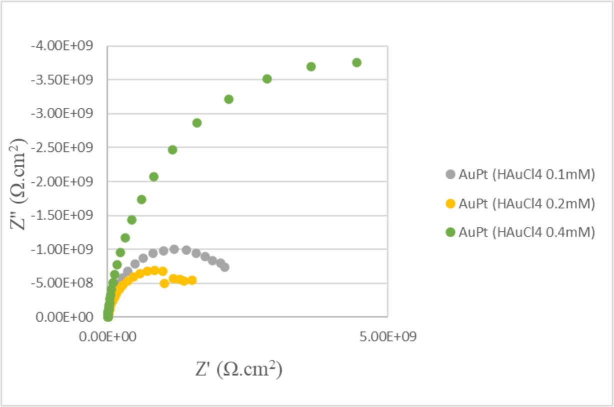

Figure 4. Nyquist plot of AuPt with varying Au ion concentration.

Figure 4 shows the EIS results of AuPt NPs with varying concentrations of Au. The more Au ions increase, the smaller the Rct produced [16]. It can be seen that AuPt with the addition of 0.2 mM Au ions is smaller than AuPt with the addition of 0.1 mM Au ions, this is because the AuPt particles (0.2 mM Au^{3+}) are more tightly distributed so that they have faster charge transfer (the resulting R_{ct} is small). Meanwhile, AuPt with the addition of 0.4 mM Au ions has a larger R_{ct} with a shape like a cauliflower, this happens because it has more surface active sites that produce higher catalytic activity. AuPt has a higher electronegativity value that encourages an increase in charge transfer from Pt to Au which causes the Pt d-orbitals to be empty and can be used for electro-oxidation reactions [10].

The catalytic performance of AuPt in the electrooxidation reaction was examined using CV. Cyclic voltametry is used to see the current density produced in the electrooxidation reaction by AuPt NPs. Electrooxidation of ethanol in this study was carried out under alkaline conditions, where the ethanol oxidation reaction has an optimum current under alkaline conditions, this is due to the presence of OH^- ions which can reduce the CO poisoning that occurs on Pt [17].

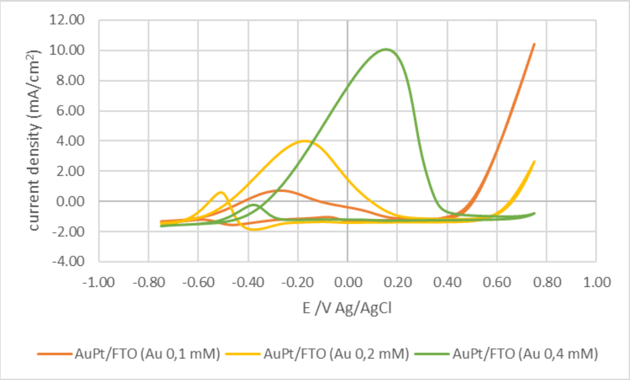

Figure 5. CV results of AuPt samples with varying concentrations of Au ions (0.1mM, 0.2mM, 0.4mM) and a fixed Pt ion concentration of 1mM during deposition.

Figure 5 shows the CV results of the AuPt sample with varying concentrations of Au ions in the ethanol oxidation reaction. This shows that the more the element Au (EDX results) in AuPt, the greater the current density produced. This happens because Au can reduce the poisoning of CO adsorbed on Pt. The poisoning of Pt by CO can inhibit the ethanol electrooxidation reaction. CO is formed from ethanol electrooxidation intermediates reaction [18]. CO will adsorb on the Pt surface so that it will block the reaction by blocking the active side of the Pt surface [19]. In the addition of Au elements in the solution, the resulting current density increases due to the increase in Au elements that can oxidize CO_{ads} on the Pt surface [18]. So that Pt can be maximized in oxidizing ethanol which causes the current density for ethanol oxidation to increase.

The ratio of current forward and backward (I_f/I_b) has been used to determine the resistance of the catalyst to CO, where if the value of the I_f/I_b ratio is large, it indicates that the synthesized material is resistant to CO very well [20]. This can be attributed to the removal of poisoning on the Pt surface by $Au\text{-}OH_{ads}$ that can convert CO to CO_2. Table 1 shows the I_f/I_b ratio values for all samples, where the AuPt sample with 0.4mM $HAuCl_4$ and 1mM K_2PtCl_6 composition has the highest I_f/I_b value of 43.53.

Table 1. I_f/I_b on each sample in ethanol electrooxidation reaction.

Sample	I_f mA/cm²	I_b mA/cm²	I_f/I_b
AuPt ($HAuPt_4$ 0.1 mM)	0.718	1.56	0.46
AuPt ($HAuPt_4$ 0.2 mM)	4.00	0.593	6.74
AuPt ($HAuPt_4$ 0.4 mM)	10.1	0.232	43.53

4. Conclusion

AuPt bimetal has been successfully synthesized via electrodeposition method. By varying the concentration of Au ions in solution, the composition and morphology of the particles can be controlled on the deposition technique used. In this study, AuPt nanocatalyst with 0.4mM Au ion concentration in electrolyte solution was shown to have good catalytic activity in ethanol electrooxidation reaction, with current density and I_f/I_b generated at 10.1 mA/cm² and 43.53, respectively. This is an implication of the large composition of Au which is known to have the ability to adsorb and oxidize CO so as to encourage an increase in current density and increase its catalytic activity.

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References

[1] L. Han, H. Ju, Y. Xu, Ethanol electro-oxidation: Cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic oscillation, *Int J Hydrogen Energy*. **37** (2012) 15156–15163. https://doi.org/10.1016/j.ijhydene.2012.08.034.

[2] J. Massing, N. van der Schoot, C.J. Kähler, C. Cierpka, A fast start up system for microfluidic direct methanol fuel cells, *Int J Hydrogen Energy*. **44** (2019) 26517–26529. https://doi.org/10.1016/j.ijhydene.2019.08.107.

[3] M.J. Giz, G.A. Camara, The ethanol electrooxidation reaction at Pt (111): The effect of ethanol concentration, *Journal of Electroanalytical Chemistry*. **625** (2009) 117–122. https://doi.org/10.1016/j.jelechem.2008.10.017.

[4] L. Demarconnay, S. Brimaud, C. Coutanceau, J.-M. Léger, Ethylene glycol electrooxidation in alkaline medium at multi-metallic Pt based catalysts, *Journal*

of Electroanalytical Chemistry. **601** (2007) 169–180. https://doi.org/10.1016/j.jelechem.2006.11.006.

[5] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.-M. Léger, Recent advances in the development of direct alcohol fuel cells (DAFC), *J Power Sources*. **105** (2002) 283–296. https://doi.org/10.1016/S0378-7753(01)00954-5.

[6] J.P.I. de Souza, S.L. Queiroz, K. Bergamaski, E.R. Gonzalez, F.C. Nart, Electro-Oxidation of Ethanol on Pt, Rh, and PtRh Electrodes. A Study Using DEMS and in-Situ FTIR Techniques, *J Phys Chem B*. **106** (2002) 9825–9830. https://doi.org/10.1021/jp014645c.

[7] L. Jiang, A. Hsu, D. Chu, R. Chen, Ethanol electro-oxidation on Pt/C and PtSn/C catalysts in alkaline and acid solutions, *Int J Hydrogen Energy*. **35** (2010) 365–372.https://doi.org/10.1016/j.ijhydene.2009.10.058.

[8] N.S. Marinkovic, M. Li, R.R. Adzic, Pt-Based Catalysts for Electrochemical Oxidation of Ethanol, *Top Curr Chem*. **377** (2019) 11. https://doi.org/10.1007/s41061-019-0236-5.

[9] L. Zhao, J.P. Thomas, N.F. Heinig, M. Abd-Ellah, X. Wang, K.T. Leung, Au–Pt alloy nanocatalysts for electro-oxidation of methanol and their application for fast-response non-enzymatic alcohol sensing, *J Mater Chem C Mater*. **2** (2014) 2707. https://doi.org/10.1039/c3tc32317j.

[10] & Ahmer.M.F. Boddula. R., Photoelectrochemical Water Splitting Materials and Applications, *Material Research Foundation*. (2020). https://doi.org/https://elib.spbstu.ru/ebsco/pdf/2386714.pdf/en/info.

[11] E. Rahmi, A.A. Umar, M.Y. Abd Rahman, M.M. Salleh, M. Oyama, Fibrous AuPt bimetallic nanocatalyst with enhanced catalytic performance, *RSC Adv*. **6** (2016) 27696–27705. https://doi.org/10.1039/C5RA27849J.

[12] Y. Wang, S. Zou, W.-B. Cai, Recent Advances on Electro-Oxidation of Ethanol on Pt- and Pd-Based Catalysts: From Reaction Mechanisms to Catalytic Materials, *Catalysts*. **5** (2015) 1507–1534. https://doi.org/10.3390/catal5031507.

[13] P. Song, S.-S. Li, L.-L. He, J.-J. Feng, L. Wu, S.-X. Zhong, A.-J. Wang, Facile large-scale synthesis of Au–Pt alloyed nanowire networks as efficient electrocatalysts for methanol oxidation and oxygen reduction reactions, *RSC Adv*. **5** (2015) 87061–87068. https://doi.org/10.1039/C5RA18133J.

[14] S. Bai, J. Jiang, Q. Zhang, Y. Xiong, Steering charge kinetics in photocatalysis: intersection of materials syntheses, characterization techniques and theoretical simulations, *Chem Soc Rev*. **44** (2015) 2893–2939. https://doi.org/10.1039/C5CS00064E.

[15] Z. Zhao, M. Zhang, X. Chen, Y. Li, J. Wang, Electrochemical Co-Reduction Synthesis of AuPt Bimetallic Nanoparticles-Graphene Nanocomposites for Selective Detection of Dopamine in the Presence of Ascorbic Acid and Uric Acid, *Sensors*. **15** (2015) 16614–16631. https://doi.org/10.3390/s150716614.

[16] A. Trani, R. Petrucci, G. Marrosu, D. Zane, A. Curulli, Selective electrochemical determination of caffeine at a gold-chitosan nanocomposite sensor: May little change on nanocomposites synthesis affect selectivity?, *Journal of Electroanalytical Chemistry*. **788** (2017) 99–106. https://doi.org/10.1016/j.jelechem.2017.01.049.

[17] H. Xu, X. Li, G. Wang, Polyaniline nanofibers with a high specific surface area and an improved pore structure for supercapacitors, *J Power Sources*. **294** (2015) 16–21. https://doi.org/10.1016/j.jpowsour.2015.06.053.

[18] D.N. Oko, Electrocatalytic Activity of Small Organic Molecules at PtAu Alloy Nanoparticles for Fuel Cells and Electrochemical Biosensing Applications, *Biosensing*. (2015). https://doi.org/http://espace.inrs.ca/id/eprint/2626.

[19] D.Y. Chung, H. Kim, Y.-H. Chung, M.J. Lee, S.J. Yoo, A.D. Bokare, W. Choi, Y.-E. Sung, Inhibition of CO poisoning on Pt catalyst coupled with the reduction of toxic hexavalent chromium in a dual-functional fuel cell, *Sci Rep*. **4** (2014) 7450. https://doi.org/10.1038/srep07450.

[20] Z. Yavari, M. Noroozifar, M. Khorasani-Motlagh, The improvement of methanol oxidation using nano-electrocatalysts, *J Exp Nanosci*. **11** (2016) 798–815. https://doi.org/10.1080/17458080.2016.1185805