

STUDY ON ELECTRO-OXIDATION OF GLYCEROL IN ALKALINE MEDIUM USING TRIMETALLIC Pt-Pd-Ni COMPOSITE ELECTRODEPREPARED ON GLASSY CARBON

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ABSTRACT

In this research, the effect of temperature and conversion of glycerol was studied by using cyclic voltammetry technique. The results showed that this reaction occurred following to diffusion mechanism with activation energy approximately of 3.44 (kcal/mol). Moreover, conversion of glycerol by electrolysis using Pt-Pd-Ni/C catalyst also was investigated and compared with the case of using pure Pt. Electrolysis process with electrode Pt-Pd-Ni/GC and pure Pt-was occurred by the first order and this result was well-suit with the previous study about the reaction mechanism of glycerol electro-oxidation process. Obtained results showed that conversion of glycerol on the trimetallic catalyst was higher than the pure Pt.

Keywords: glycerol, oxidation, electrode, trimetallic, diffusion mechanism, conversion.

1. INTRODUCTION

The electro-oxidation of alcohol is a research topic of great importance to the development of high-performance alcohol fuel cells. The direct alcohol fuel cell appears to be a promising system because the alcohol used is not reformed into hydrogen gas, but oxidized directly in the cell. Included in a group of alcohol for fuel cell is glycerol. The growth of world biodiesel production has caused a surplus of glycerol, which is generated as a byproduct of the process [1]. Therefore, the research of glycerol conversion for fuel cell application, which aims to increase the performance of cells and close green energy cycle, are attractive to many groups of scientists in the world. However, there are many troubles need to be tackled due to the difficulty of comparing electro-oxidation glycerol with methanol [2 - 3]. Many types of research proved that the oxidation glycerol and other alcohols in alkaline media are faster and stronger when using Pt, Au, Pd as catalysts [1, 3 - 5]. However, the high cost and easily poisoned when using them as catalyst for fuel cells are two big troubles of noble catalysts, hence, prevented the widely application of fuel cells in industry. The content of Pt and Pd in catalytic materials could

be reduced by synthesizing modified their materials on conductive substrate or building composite materials which involve noble metals with other non-noble metals [5 - 8]. Due to this reason, the hot trend in this field now is synthesizing the composite materials (with or without Pt) to reduce cost but still remain the activities. Among non-noble metals which are used to replace platinum, palladium and nickel got much more attention than others [6 - 9]. The research shows that Ni has good catalytic activities for oxidation alcohol in alkaline media, that is based on redox potential $\text{Ni}^{3+}/\text{Ni}^{2+}$ in alkaline media is belong in range of 0.36 V to 0.44 V (SCE), is quite close with the oxidation potential of alcohol in alkaline media. However, when comparing with noble metal catalysts, the activity of Ni is much lower. Hence, to improve the activity of the catalyst for oxidation alcohol in alkaline media, the catalyst materials, which contain Ni, was synthesized by co-electrodeposition with noble metals.

Our previous research has shown that the trimetallic composite electrode catalysis Pt-Pd-Ni/GC has higher catalytic activity than pure Pt, Pd and bimetallic material Pt-Pd/GC [6]. However, in order to optimize the process of electrode fabrication, as well as to find appropriate conditions for electrolytic oxidation of glycerol to be highly effective, in this study, we first investigated the mechanism and determination of glycerol conversion during electrochemical oxidation of glycerol in the alkaline medium on Pt-Pd-Ni/GC electrode system.

2. EXPERIMENT

2.1. Chemical

Na_2PdCl_4 (Aldrich), K_2PtCl_4 (Aldrich), $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Merck), $\text{C}_3\text{H}_5(\text{OH})_3$ (Merck), KOH (Merck), H_2SO_4 (Merck), H_3BO_3 (type AR-China), NaCl (type AR-China).

2.2. Method to preparation electrode catalyst

Glassy carbon (GC) electrode was polished by smooth sandpaper (type C-2000), then treated in ultrasonic and cleaned by pure water to enhance the adhesive ability of metal onto substrate. Then the GC electrode was activated by scan several times (from -1.8 V to 1.8 V, scan rate 50 mV/s) in H_2SO_4 1M until the voltammogram was stable. Finally, the trimetallic electrode based on Pt, Pd and Ni was synthesized by electrodeposition method with the condition, which shown in work [6].

2.3. Investigation method

The electrochemical properties of material were measured in a three electrode system: reference electrode (Ag|AgCl|KCl 3M), counter electrode (Pt), and working electrode. All electrochemical experiment was performed in a potentiostat-ganvanostat Autolab 30 (Netherlands) at Faculty of Chemistry, VNU – University of Science.

3. RESULT AND DISCUSSION

3.1. Study the effect of temperature and the mechanism of electro-oxidation glycerol

The cyclic voltammogram of Pt-Pd-Ni/GC electrode in solution KOH 1M, containing glycerol 1M at different temperatures is shown in Fig. 1. The result pointed out that, as the temperature rises, the current density rises and the oxidation potential is shifted to more positive

positions. These phenomena could be explained as follow: with increasing temperature, the conductivity of the alkaline solution grows and the viscosity of the solution decreases, resulting in the fact that glycerin is more easily diffused to the surface of electrode. Moreover, when the temperature increases, the kinetics of the reaction proceeds faster, the C-C bond is more easily destroyed. From the voltammogram given below, it can be seen that the activity of catalyst is stable from 25 °C to 55 °C.

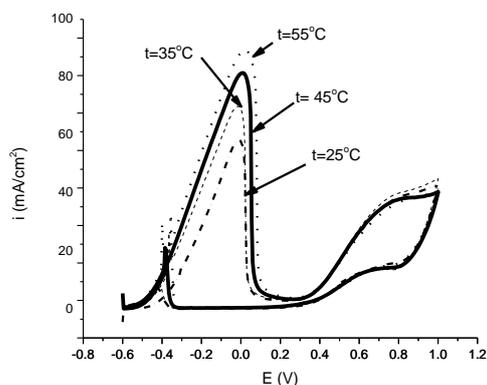


Figure 1. Cyclic voltammogram of Pt-Pd-Ni in solution KOH-1M containing glycerol 1M at different temperature.

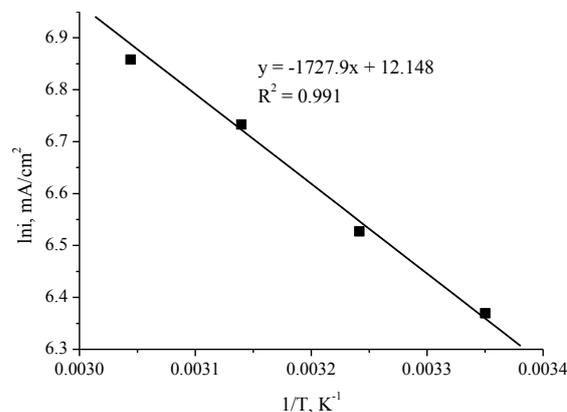


Figure 2. Temperature dependence of current density in electro-oxidation process of glycerol on Pt-Pd-Ni/GC electrode.

One of the most important goals of studying the electrochemical properties of materials is determining the reaction kinetics, which was catalyzed by electrode material. Current researches are inconsistent in conclusion about electro-oxidation glycerol reaction. In this study, we initially investigated the mechanism of electro-oxidation glycerol in alkaline media based on trimetallic catalyst. To get insight into the mechanism of glycerol electro-oxidation on the electrode, the activation energy of this process were calculated by Arrhenius equation:

$$i = i_0 \exp\left(\frac{-E^*}{RT}\right)$$

i : current density; i_0 : constant; E^* : activation energy (J/mol); T : absolute temperature (K); R : gas constant ($R=8.314$ J/K.mol).

It is known that the activation energy of the electrooxidation process for the diffusion kinetics is from 2.0 kcal / mol to 6.0 kcal / mol [10]. Fig. 2 shows that the temperature dependence of the oxidation of glycerol in the alkaline solution at the Pt-Pd-Ni / GC electrode is performed as linear functions. The activation energy of electro-oxidation can be calculated, this value is approximately 3.44 (kcal.mol⁻¹). This value is the first evidence to prove the diffusion kinetics of glycerol electro-oxidation [10].

Other of the methods for evaluating the mechanism of electrochemical reactions is investigating the dependence of current density on scan rate. In Fig. 3 shows cyclic voltammogram of Pt-Pd-Ni/GC electrode in solution containing glycerol 1M - KOH 1M at different scan rates and the calibration curve between peak height and square root of scan rate.

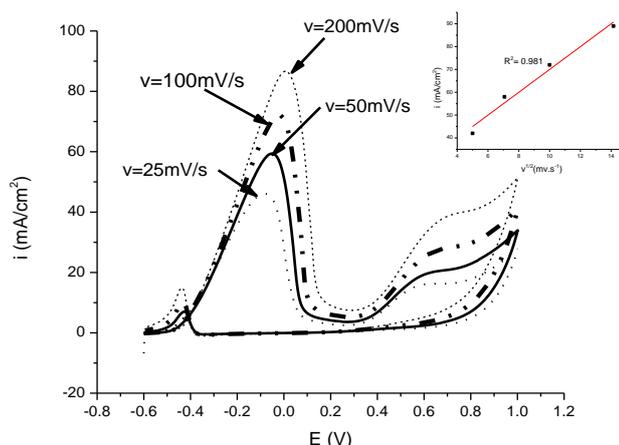


Figure 3. Cyclic voltammogram of Pt-Pd-Ni/GC electrode in solution containing glycerol 1M - KOH 1M at different scan rates.

The results showed that the calibration curve, which describes the relation between oxidation peak and square root of scan rate, had linear form. Hence, we can conclude that the process of oxidation glycerol on catalyst materials was controlled by the material transfer process from solution to surface of electrode (according to diffusion kinetics) [10].

3.2. Influence of electrooxidation time to glycerol conversion.

One of the important properties of an electrochemical catalyst is its ability to convert fuel. In this study, we investigated the conversion of glycerol in an alkaline medium to Pt-Pd-Ni / GC by the electrolyzed solution with an electrolytic potential as oxidation peak. The residual concentration of glycerol in the solution after electrolysis was determined by the cyclic voltammetry method with working electrodes Pt. The conversion of glycerol depends on electrolysis time, catalytic activity and stability of electrode material. To evaluate concentration of the glycerol, the study was followed by the procedure: calibration curve of glycerol was built, then determine the residual concentration of glycerol in solution with calibration curve. The calibration curve, which describes the relationship between the value of oxidation peak height and concentration of glycerol, was shown in Fig. 4.

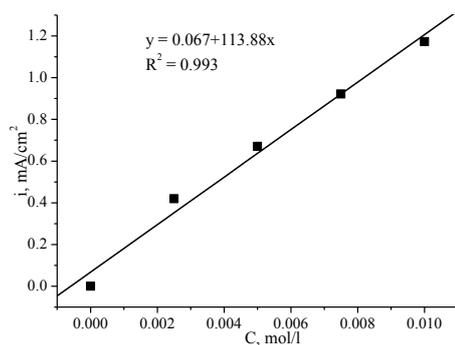


Figure 4. Calibration curve of oxidation peaks with glycerol concentration.

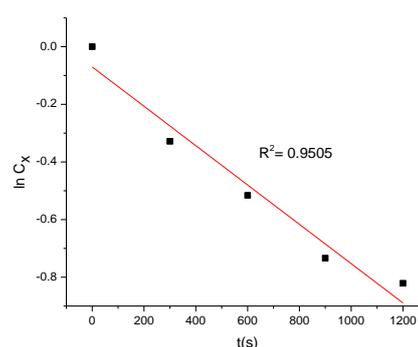


Figure 5. The curve describes the relation of $\ln C_x$ versus time with using Pt-Pd-Ni/GC electrode.

The conversion of glycerol was calculated and showed in Table 1. The result showed that trimetallic electrode had better activities comparing to pure Pt electrode. This could be explained by the combination of catalytic activities of each metal and the stability of this composite material. Studying the dependence of $\ln C_x$ versus electrooxidation time when using trimetallic electrode, the result showed that it had a linear form (Fig. 5). The same result was obtained with using Pt-pure. Therefore, process electrolysis with electrode Pt-Pd-Ni/GC and Pt-pure was occurred by first order:

$$\ln C_x = -kt + \ln C_0 \Rightarrow k = \frac{1}{t} \ln \frac{C_0}{C_x}$$

k - rate constant of reaction electrolysis; t – electrolysis time; C_0 – concentration of glycerol at the start of the reaction; C_x - concentration of glycerol after electrolysis.

Table 1. The conversion of glycerol versus time when using Pt-Pd-Ni/GC and Pt pure electrode.

Time of electrolysis	Pt-Pd-Ni/GC		Pt-pure	
	Concentration, mol/l	Conversion, %	Concentration, mol/l	Conversion, %
0	1.00		1.00	
300	0.72	28	0.81	19
600	0.60	40	0.76	24
900	0.48	52	0.68	32
1200	0.45	55	0.65	35

The rate of electro-oxidation reaction on Pt-Pd-Ni/GC and Pt-Pure electrodes depends only on the concentration of glycerol, the exchange electron process is very fast, in another word the diffusion kinetics plays a key role in this reaction. The result was well-suit with the previous study of the kinetics of this reaction.

Table 3. Rate constant of glycerol electro-oxidation reaction at different electrode.

Electrode material	Rate constant (mol.l ⁻¹ .s ⁻¹)
Pt-Pd-Ni/GC	6.83.10 ⁻⁴
Pt-pure	3.41.10 ⁻⁴

Table 3 shows that the rate of electro-oxidation reaction of glycerol with using Pt-Pd-Ni/GC electrode is faster than using Pt-pure. The obtained results were consistent with the results shown in Table 2 and in the analysis cyclic voltammogram [6].

4. CONCLUSION

In summary, cyclic voltammetry method studied process electro-oxidation of glycerol in alkaline solution with using trimetallic composite electrode (Pt-Pd-Ni/GC) and Pt-Pure. The obtained results showed the reaction electro-oxidation of glycerol using trimetallic and Pt-pure

electrodes occurred via diffusion kinetics and at first order. The trimetallic electrode had better activities when compared to pure Pt electrode.

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