

ELECTROCHEMICAL OXIDATION OF GLYCEROL USING GOLD ELECTRODE

(Pengoksidaan Elektrokimia Gliserol Secara Elektrokimia Menggunakan Elektrod Emas)

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Abstract

Cyclic voltammetry, potential linear V and chronocoulometry methods were carried out to gain electrochemical behavior of glycerol at a gold electrode. Potassium hydroxide and sulfuric acid were chosen to be the electrolyte for the electro-oxidation of this organic compound. Besides gold plate electrode, gold composite electrode (Au-PVC) was also used as the working electrode. The Au-PVC composite electrode was characterized by Scanning Electron Microscopy (SEM) to determine its morphological aspects before and after used in electrochemical oxidation of glycerol. In alkaline solution, the adsorption of hydroxide species onto the surface of both gold plate and composite Au-PVC electrodes occurs at potential around 500 mV vs SCE. However, at gold plate electrode, there was a small, broad peak before the drastic escalation of current densities which indicates the charge transfer of the chemisorbed OH^- anion. In acidic media, the gold oxide was formed after potential 1.0 V. From the cyclic voltammogram glycerol undergo oxidation twice in potassium hydroxide at gold plate and Au-PVC composite electrodes, while in sulfuric acid, oxidation reaction happened once for glycerol on the gold plate electrode. Overall, electrochemical oxidation of glycerol was more effective in alkaline media. Tafel graph which plotted from potential linear V method shows that Au-PVC composite electrode is better than gold plate electrode for the electro-oxidation of glycerol in alkaline solution. Electrochemical oxidation of glycerol products as analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) produced several carboxylic acids and phenolic compounds.

Keywords: electrochemical oxidation, glycerol, carboxylic acid, phenolic compounds

Abstrak

Kaedah voltammetri kitaran, keupayaan linear V dan kronokuolometri telah dijalankan bagi mengetahui kelakuan elektrokimia sebatian gliserol pada elektrod emas. Kalium hidroksida dan asid sulfurik telah digunakan sebagai elektrolit bagi pengoksidaan elektrokimia sebatian organik tersebut. Selain elektrod kepingan emas, elektrod komposit emas polivinil klorida (Au-PVC) juga digunakan sebagai elektrod kerja (anod). Morfologi elektrod komposit Au-PVC dicirikan dengan Mikroskop Imbasan Elektron (SEM). Dalam larutan alkali, penjerapan sebatian hidroksida pada elektrod kepingan emas dan elektrod komposit Au-PVC berlaku pada keupayaan ± 500 mV. Walau bagaimanapun, pada elektrod kepingan emas, terdapat satu puncak lebar yang kecil sebelum peningkatan drastic arus yang dikaitkan dengan pemindahan cas separa anion OH^- yang terjerap secara kimia. Dalam larutan berasid, oksida emas terbentuk selepas keupayaan 1.0 V. Berdasarkan voltammogram berkitar gliserol mengalami dua kali pengoksidaan dalam larutan kalium hidroksida pada elektrod kepingan emas dan elektrod komposit Au-PVC. Manakala dalam larutan asid sulfurik, tindak balas pengoksidaan hanya berlaku sekali. Secara keseluruhannya, pengoksidaan elektrokimia gliserol adalah lebih berkesan dalam larutan alkali. Graf Tafel yang diplot melalui kaedah keupayaan linear V menunjukkan bahawa elektrod komposit Au-PVC merupakan elektrod yang lebih baik berbanding elektrod kepingan emas bagi pengoksidaan elektrokimia dalam medium beralkali. Hasil pengoksidaan elektrokimia gliserol yang dianalisa menggunakan Kromatografi Gas-Spektrometer Jisim mendapati produk yang terhasil adalah asid karboksilik dan sebatian fenol.

Kata kunci: pengoksidaan elektrokimia, gliserol, asid karboksilik, sebatian fenol

Introduction

Production of biodiesels as an alternative to conventional power sources such as petroleum has attracted researches all over the world in recent years. However, the concern is on the major byproduct of the biodiesels production which is glycerol, $\text{HOCH}_2\text{CHOHCH}_2\text{OH}$. The excess glycerol generated may become an environmental problem, since it cannot be disposed off in the environment [1]. Moreover, conventionally oxidation of glycerol with mineral acids in producing tartaric acid or nitric acid yields glyceric acid which is harmful to the environment [2]. Thus, glycerol oxidation by means of heterogeneously catalysis is an environmentally friendly alternative for producing a large number of products [3, 4].

Electrode modified by gold substrate was found to exhibit high electro catalytic activities for the oxidation of glycerol than that with the glassy carbon substrate and many product like glyceraldehyde, glyceric acid, dihydroxyacetone, tartronic acid, hydroxypyruvic acid, glycolic acid, oxalic acid and mesoxxalic acid were produced [5]. The mechanism for electrooxidation of glycerol suggested was as summarised in Figure 1 [6]. Selective oxidation of glycerol with air/oxygen is always carried out in the liquid phase using water as the solvent [7]. In acidic condition, secondary alcohol functional will take place whereas basic solution promotes the oxidation of the primary alcohol functional [8]. In the past few years, the electrodes those which are of specific interest are composites of insulating organic polymers filled with electrical conductors: metallic particles, carbon powders or metallic oxides [9].

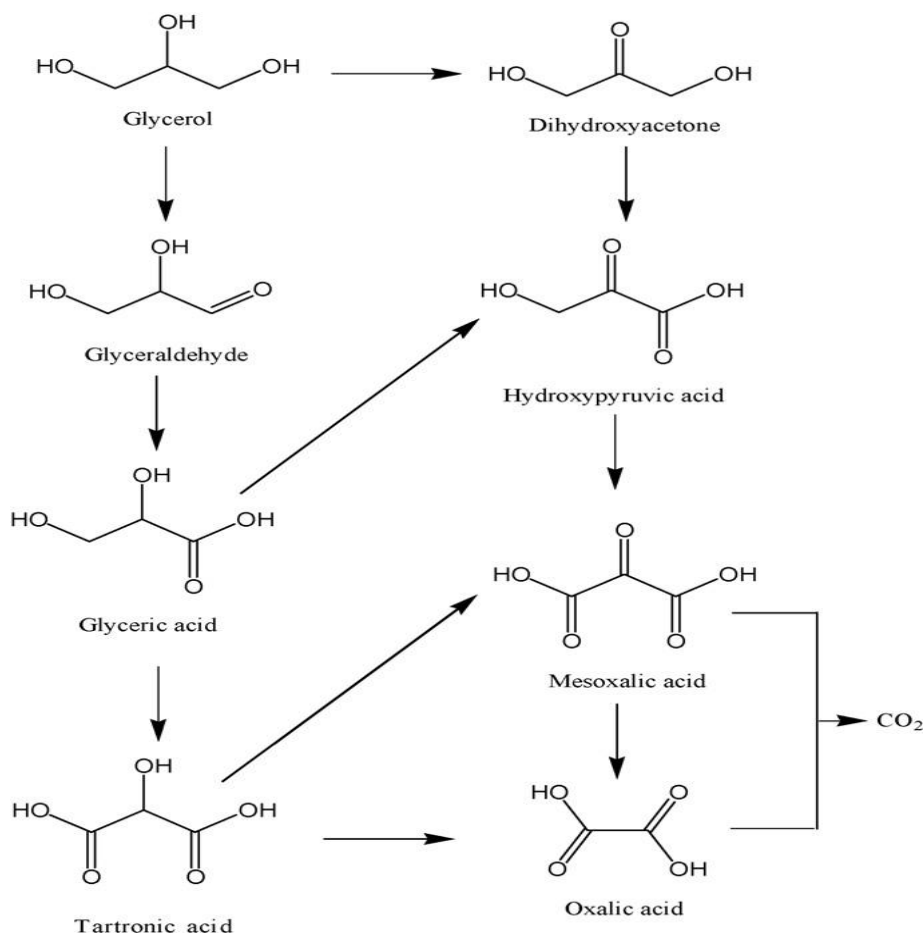


Figure 1. Suggested mechanism for the electrooxidation process of glycerol

Composites electrode offer many potential advantages compared to more traditional electrodes consisting of a single conducting phase such as glassy carbon, platinum or gold. Advantageous characteristics of these electrode materials are the improvement in signal-to-noise ratio, high mechanical resistance, good stability in flowing systems and relative simplicity in preparation and surface renewal [10]. This particular paper studies the electrochemical behavior of glycerol electrooxidation at Au-PVC composite electrode in comparison with Au plate electrode as a working electrode.

Materials and Methods

Reagents

Sulphuric acid (H_2SO_4), perchloric acid (HClO_4) and glycerol ($\text{C}_3\text{O}_3\text{H}_7$) were purchased from Sigma and used without further purification. Both acids solution was prepared by dissolving the reagent in deionized distilled water.

Preparation of working electrode

PVC-Au pellet was prepared by mechanical alloying technique as already published elsewhere [11, 12]. Gold powder (Aldrich Chemical Company) was mixed with poly (vinyl chloride) in ratio of 95:5 percent respectively. The mixture was then homogenized for three to four hours. Approximately 5 mL of tetrahydrofuran (THF) solvent was added and swirled flatly to dissolve the PVC in the solution prior being dried in an oven for three hours (100°C). The composite powder obtained then was pressed into pellet under a pressure of 10 tonne/cm^2 . The pellet was stick to a silver wire (in a glass rod) with silver conductive paint. Subsequently, epoxy glue was applied to cover the unwanted surface (joining surface). Au plate electrode was prepared using a solid Au metal foil (99.99% purity, Aldrich Chemical Company) [13]. A 0.5 mm thick Au foil was cut into approximately $1 \text{ cm} \times 1 \text{ cm}$ piece and connected to silver wire with silver conducting paint prior covered with epoxy gum.

Electrochemical measurement

Universal Pula Dynamic EIS, Voltammetry, Voltalab potentiostat (Model PGZ 402) complete with Voltamaster 4 software was used for electrochemical measurement. All experiments were carried out at room temperature. The cyclic voltammetry experiment and electrolysis were performed using three electrodes system: Au-PVC or Au plate as a working electrodes (anodes), platinum wire and Saturated Calomel Electrode (SCE) as an auxiliary and reference electrode respectively in a single undivided electrochemical glass cell with capacity of 50 mL. Electrolysis of glycerol was carried out at 0.4 V vs SCE for 5 h. High purity nitrogen gas was used for deaeration at least 10 minutes prior to each run and to maintain nitrogen blanket during the measurements.

Characterization of electrochemical oxidation products

Electrolysis products were characterized using Gas Chromatography-Mass Spectrometer, GC-MS. In order to discard the contaminants and to preconcentrate the samples, electrolysis product was extracted using acetonitrile prior analysis.

Results and Discussion

Alkaline medium

Glycerol oxidation in alkaline medium showed that both gold and platinum are electroactive, particularly gold which gives much higher current densities [14]. High current density in an electrochemical cell produces more electrons which gives rise to the overall rate of reactions [15]. Figure 2 shows the cyclic voltammogram of Au plate and Au-PVC electrodes in potassium hydroxide solution and glycerol. Despite having two oxidation peaks for both electrode (at potential around 400 mV vs. SCE during positive sweep and around 100 mV vs. SCE during negative sweep), glycerol oxidized with high current density. At concentration of 0.20 M, electrochemical oxidation of glycerol reaches current density up to the value of 8 mA/cm^2 .

In order to study the effects of concentration on the current density, a series of concentration ranging from 0.04 M to 0.20 M of glycerol in the KOH solution were put in a test. As expected, the current densities become higher with the increase of the concentration of glycerol for both oxidation peaks. However, the peaks are shifted to more positive potential.

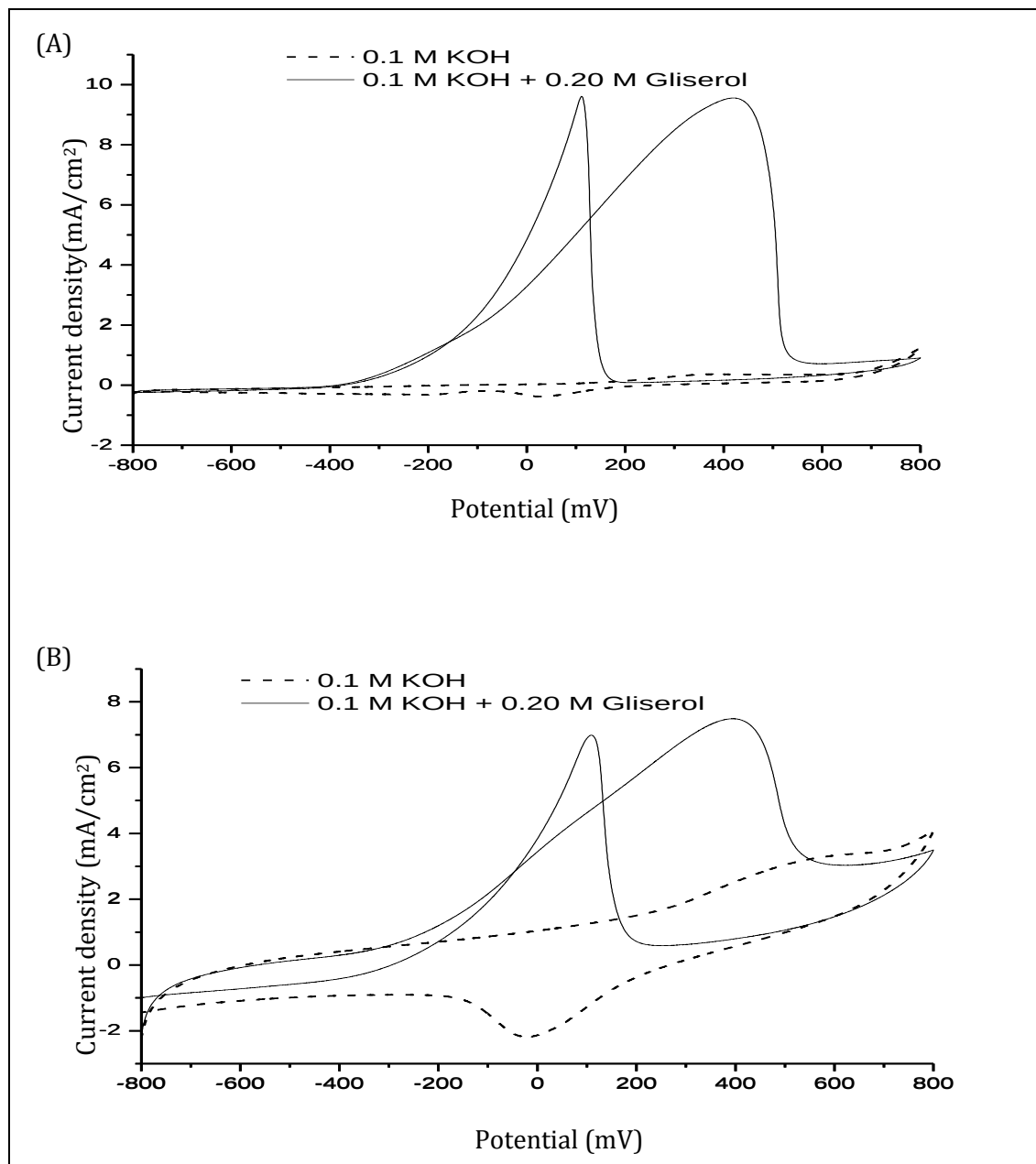


Figure 2. Cyclic voltammogram of Au plate (A) and Au-PVC (B) electrodes in 0.1 M KOH (- - -) and 0.1 M KOH + 0.20 M glycerol (----). Scan rate = 50 mV/s

Acidic medium

The electrochemical behavior of glycerol electro oxidation at an Au and Au-PVC electrode was also studied in acidic solution where without and with 0.20 M glycerol was added to 0.08 M sulphuric acid and voltammetry method was used to produce cyclic voltammogram (Figure 3). The voltammogram shows the appearance of a new peak around 1.15 V vs. SCE when glycerol was added to the acidic solution (dash line).

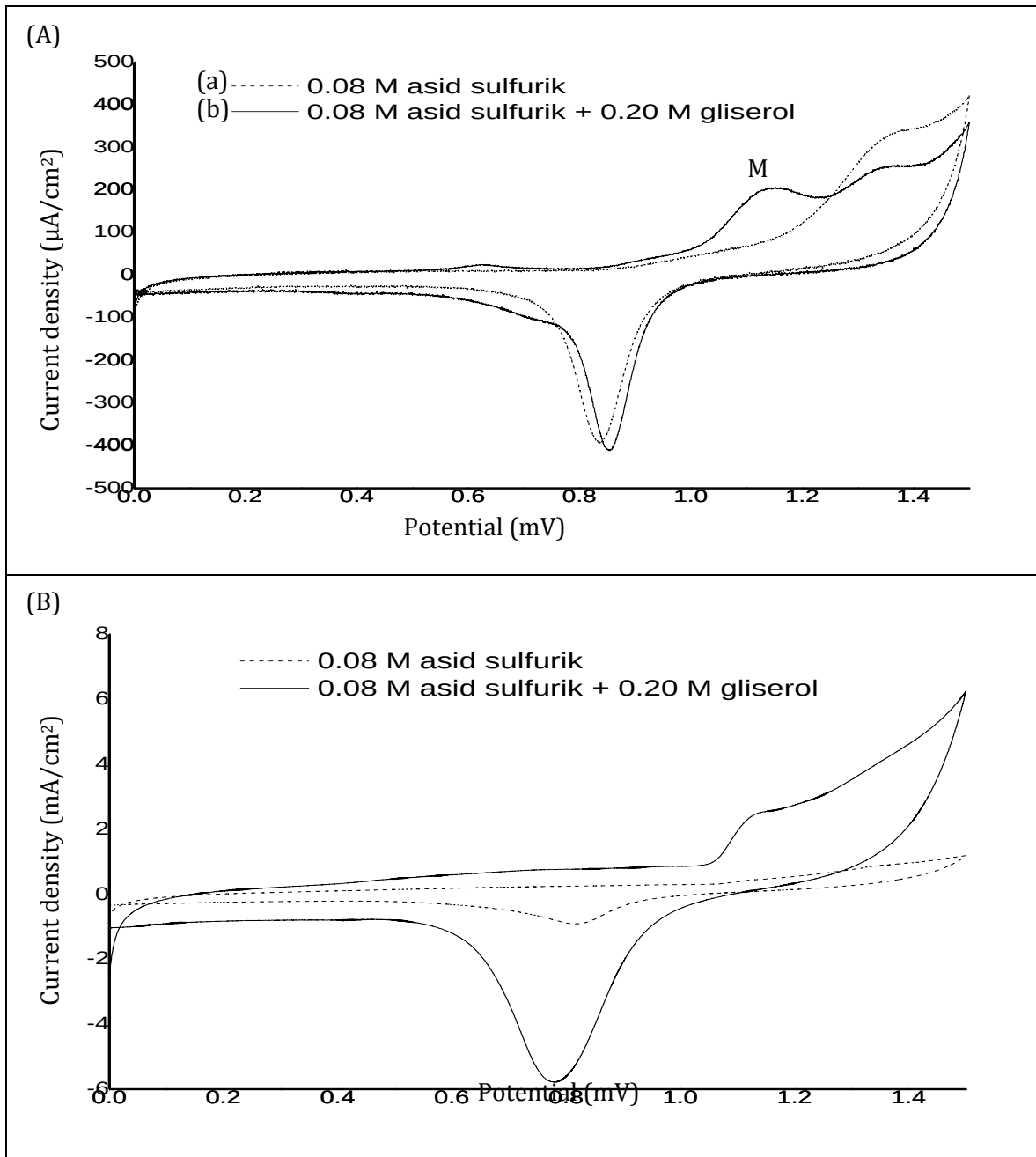


Figure 3. Cyclic voltammogram of Au (A) Au-PVC (B) electrodes in 0.08 M H₂SO₄ and 0.08 M H₂SO₄ + 0.20 M glycerol. Scan rate = 50 mV/s.

A concentration test was conducted by adding up the glycerol concentration up to 0.20 M into the sulphuric acid solution. There is no change of the cyclic voltammogram when 0.04 M glycerol was added but the oxidation peak of glycerol appears at the concentration of 0.08 M and continuously higher with the next addition of glycerol concentration as summarized in Table 1.

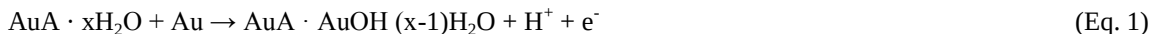
Table 1. Linear equation for glycerol using Au plate and Au-PVC electrodes in both alkaline and acidic medium

Electrode	Medium	Linear Equation	
		First Peak	Second peak
Au Plate electrode	Alkaline (0.1 M KOH)	$y = 28.55x + 4.48$ ($R^2 = 0.903$)	$y = 16.77x + 6.48$ ($R^2 = 0.965$)
	Acidic (0.8mM H ₂ SO ₄)	$y = 0.70x + 0.07$ ($R^2 = 0.960$)	
Au-PVC Composite electrode	Alkaline (0.1 M KOH)	$Y = 16.70x + 4.54$ ($R^2 = 0.863$)	$23.57x + 2.76$ ($R^2 = 0.844$)
	Acidic (0.08M H ₂ SO ₄)	$Y = 9.51 + 0.76$ ($R^2 = 0.944$)	

Comparison between gold plate (Au) electrode and gold composite (Au-PVC) electrode in both acidic and alkaline medium

Although there are not much different in current densities for both electrode, but the cyclic voltammogram for glycerol in alkaline medium using Au-PVC electrode show a better shape, then the Au-PVC electrode was chosen for further analysis. In term of supporting electrolyte, alkaline medium is much more superior compare to acidic medium (Table 1). Tafel plot test carried out also shows that Au-PVC composite electrode was better than the Au electrode.

Oxidation peak for Au occur at a potential above 0 V vs. SCE (Equation 1), where at the earlier stage involving the discharging of water molecule which adsord together with anion at electrode surface [16, 17].



Characterisation of oxidation product

Due to their cyclic voltammetry behavior in both acidic and alkaline supporting electrolyte at both electrode, electrochemical oxidation of glycerol was then carried out in alkaline medium and composite electrode (Au-PVC) as a working electrode. The possible compound produced are hydroxyaseton, hydroxypyruvic acid, glyceric acid, glycolic acid, mesooxalic acid, oxalic acid and tartronic acid [8]. GC-MS was used to identify the electrochemical oxidation product of glycerol with acetonitrile as a solvent. With the electrolysis time of 5 hours. in 0.1 M KOH at 0.4 V vs SCE. Base on the GC-MS spectrum obtained the products analysed were containing the mixture of carboxylic acid and phenolic compounds (Figure 4).

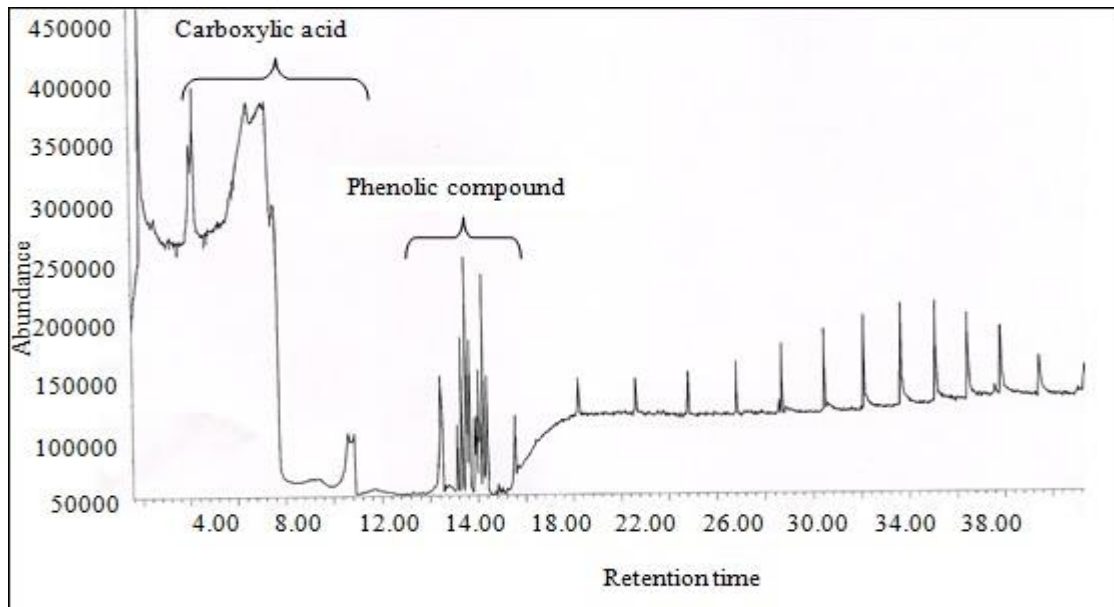


Figure 4. GC-MS Chromatogram for electrooxidation product of glycerol

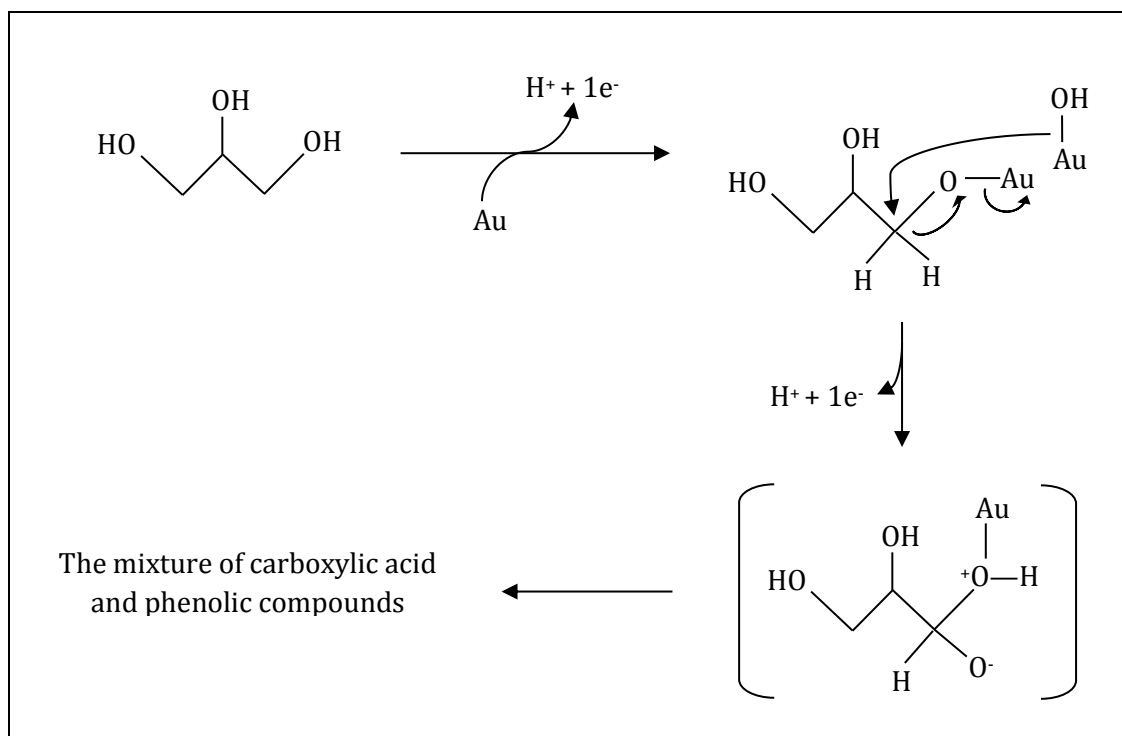


Figure 5. Suggested mechanism for the electrochemical oxidation of glycerol without the flow of hydrogen and oxygen gases

Although gold has been identified as a versatile catalyst, but more questions about active species about gold during reactions arise [18, 19]. For oxidation of diol in aqueous solution, gold was found to be active and selective for primary alcohols where oxidation of glycerol involving hydrogen and oxygen may produce a variety of compounds such as glyceraldehyde, glyceric acid, tartronic acid, dihydroxyacetone, hydroxypyruvic acid and mesosalic acid [3, 7, 20]. The mechanism involve for electrochemical oxidation of glycerol in KOH without the flow of hydrogen or oxygen gases that may produce the mixture of carboxylic acid and phenolic compounds could be suggested as summarised in Figure 5.

Conclusion

The results show that glycerol is more actively oxidized in alkaline solution at modified gold composite electrode and the electrochemical oxidation of glycerol may produce a mixture of carboxylic acid and phenolic compounds.

Acknowledgement

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