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PRODUCTION OF ACETIC ACID FROM ETHANOL BY ELECTROLYSIS (ELECTROSYNTHESIS)

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ABSTRACT

Production of acetic acid from ethanol by electrolysis (electrosynthesis) in alkaline (0.008 M KOH) and acidic (0.08 M $HClO_4$) mediums has been carried out using platinum wire electrode. Besides that, the electrochemical study by cyclic voltammetry (CV) in different scan rates and electrolyte (alkaline and acidic mediums) also had been done. The study shows that the oxidation potential of ethanol ranges from 600-1065 mV in 0.008 M KOH and 700-1125 mV in 0.08 M $HClO_4$. The electrooxidation products were analyzed using the High Performance Liquid Chromatography (HPLC).

Keywords: Ethanol, acetic acid, electrolysis, electrosynthesis.

1. INTRODUCTION

Acetic acid is an important commodity used in some industries, with about 6 million tons of world demands per year. The primary use of this chemical is in the manufacture of assorted acetate esters, fungicide and also as a solvent for many organic compounds, the preparation of pharmaceuticals products (e.g. aspirin), cellulose acetate that is important in making film and plastic wares, perfumes and synthetic fiber [16].

The first carbonylation process involving the changes of methanol towards acetic acid was commercialized in 1960 by BASF. It used iodide promoted cobalt catalyst plus a very high pressure (600 atm) and temperature (230^0C), producing acetic acid in ca. 90% selectivity. While the production of acetic acid by the Monsanto process needs alkaline medium, rhodium catalyst and only operates at the pressure between 30-60 bars and temperature of 150-200^0C. This process can gives a selectivity of over 99% using methanol as its main ingredient. The production of acetic acid using the iridium catalyst system has been commercialized in 1996 by BP-Amoco. This process was known as "Cativa™" process [12]. Synthesis of acetic acid by direct oxidation of ethylene in alkaline medium using catalysts was studied by Wang et al., [14].

Among the other process mentioned above, the process that was still being used until now for the production of acetic acid from methanol is the Monsanto process. This process can either involved reactions of ordinary chemistry or organic synthesis conventionally. Unfortunately, it has many weaknesses. Consequently, the production of acetic acid by electrochemical process or known as electrosynthesis was proposed. Among all the advantages of electrosynthesis that had been found, the most important thing is that a very wide range of oxidation and reduction reaction is possible. Other advantages are: less energy required, it is less hazardous, eliminating or minimization of polluting by products that requiring disposal, great chances of reaching a higher level of product purity and selectivity, considerably improved capital and operating cost over conventional methods [15].

Recently, a new electrooxidation of ethanol for application in fuel cells system and study of electrochemical oxidation of ethanol was developed [1,2,4,10,11,13]. Those studies may probably lead to the design of catalyst for an effective oxidation of such organic molecule and its use as fuel for low temperature fuel cells. Nevertheless, in spite of an incomplete oxidation, the use of ethanol can be an advantage because such oxidation products can be either acetaldehyde or acetic acid depending on the reaction conditions. These products have a very high commercial interest. Ethanol does not easily evaporate at room temperature, not readily oxidized, non toxic and easily available from biomass resources [7,8].

Researches on ethanol electrooxidation for fuel cell and the studies on its mechanism reactions have been done by many researchers, but nobody has ever done the research on the ethanol electrooxidation for the electrosynthesis of acetic acid. In this work we studied the ethanol electrooxidation to acetic acid using platinum wire electrodes in both alkaline and acidic mediums. Platinum (Pt) is known as an inert metal with a strong catalytic for many electrochemical reactions. Many components can be adsorbed on Pt surfaces and the adsorption of hydrogen is a well known phenomenon in electrochemistry. The effect of electrolyte, the time of electrolysis, concentration of ethanol and its oxidation potential was also being studied. These electrochemical oxidations products were confirmed by HPLC.

2. EXPERIMENTAL

2.1 Solution and instrumentation

All solutions were prepared by dissolving its analytical-reagent grade (Merck) compound in deionised distilled water and. Both 1.0 M $HClO_4$ and 0.1 M KOH were used as the supporting electrolyte. Nitrogen was used to deareate the solutions for 10 minutes and to keep an inert atmosphere over the solution. Ethanol solutions were prepared by dilution of absolute ethanol (BDH laboratory supplies) with deionised water.

Universal Pulsa Dynamic EIS, Voltammetry, Voltalab potentiostat (Model PGZ 402) was used for electrochemical measurements while data acquisition was accomplished by using the Voltamaster 4 software. Voltammetric experiments were done in a three electrodes system using a platinum wire as working electrode, an Ag/AgCl (KCl saturated) or SCE reference electrode and a platinum wire as the counter electrode. All the potentials given are with respect to the SCE reference electrode.

Analyses by the High Performance Liquid Chromatography (HPLC) were carried out using an equipment comprised of a pump (Waters 1515 Isocratic HPLC Pump), a column (C18) and two detectors which are an UV-visible detector (Waters 2487, Duel λ Absorbance detector) and a differential refractometer set on line. Chromatograms were recorded and integrated by an integrator-calculator (Merck-Hitachi D-2500). All experiments were carried out at room temperature. The mobile phase of acetonitrile in 0.1% H_3PO_4 was applied.

2.2 Experimental procedure

The electrolysis process was performed in a solution of 0.45 M ethanol in 0.008 M KOH or 0.08 M $HClO_4$ at room temperature. The electrochemical studies by cyclic voltammetry (CV) and oxidation of ethanol by potentiostatic method were performed in a glass electrochemical cell with a platinum wire counter and working electrodes. The potential of the working electrodes was measured against a SCE reference electrode. Electrolysis samples were analyzed by the High Performance Liquid Chromatography (HPLC).

3. RESULT AND DISCUSSION

3.1 Oxidation of ethanol in alkaline medium

Before running the electrolysis, cyclic voltammetry was used to check the reactivity of ethanol on platinum wire in two different mediums, perchloric acid and potassium hydroxide. The voltammograms allowed a choice of the convenient potential range to obtain a suitable oxidation potential. Fig. 1a-1b presents the voltammograms of 0.1 M KOH and 0.01 M KOH respectively using platinum wire as the working electrode without (a) and with ethanol (b).

Figure 1b shows that the oxidation of ethanol occurred at potential range of -250 mV-1600 mV where two peaks can be observed. First peak is at 600-1065 mV. This peak designate the oxidation process of ethanol by the following reaction mechanism as suggested by Periera, et al., (2004) and Filho, et al., (1998):

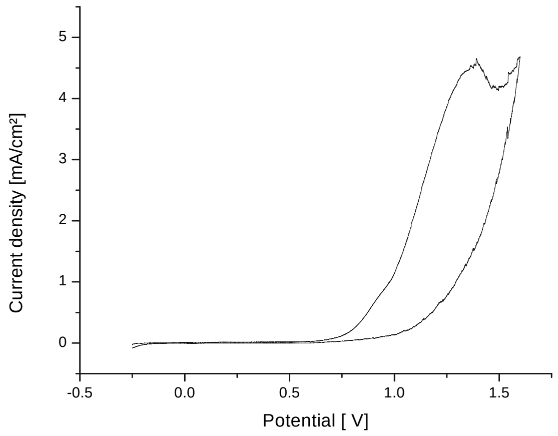
$$CH_3CH_2OH + 4OH^- \longrightarrow CH_3COOH + 3H_2O + 4e^-$$
$$CH_3COOH + CH_3CH_2OH \longrightarrow CH_3COOCH_2CH_3 + H_2O$$

From the above reaction, we can see that ethanol electrooxidation will produced acetic acid and ethyl acetate. The acetic acid forming process was suggested by Xia, et el., (1997). The reaction mechanisms on the Pt electrode surface are as the following:

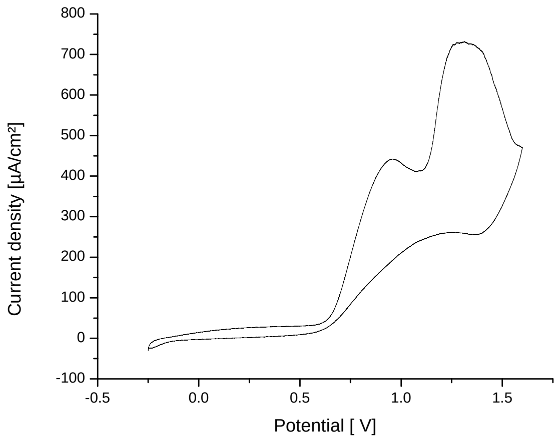
$$C_2H_5OH + Pt(H_2O) \longrightarrow Pt\,(C_2H_5OH) + H_2O$$

$$PtC_2H_5OH + Pt \xrightarrow{-xH^+,\ -xe^-} Pt\,(CO) + Pt(res)$$
$$Pt(C_2H_5OH) \longrightarrow Pt\,(CH_3CHO) + 2H^+ + 2e^-$$
$$Pt(H_2O) \longrightarrow Pt\,(OH) + H^+ + e^-$$
$$Pt\,(CH_3CHO) + Pt\,(OH) \longrightarrow CH_3COOH + H^+ + e^- + 2\,Pt$$

$$Pt(CO).Pt(res) + Pt(OH) \xrightarrow{-xH^+,\ -xe} CO_2 + Pt$$



(a)

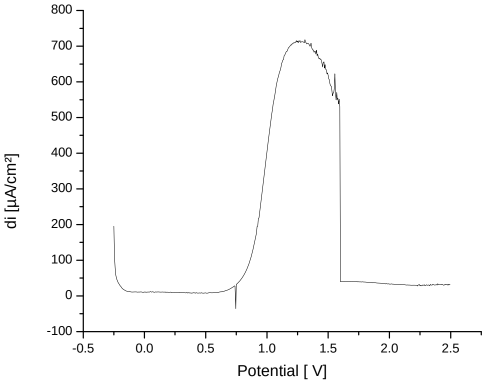


(b)

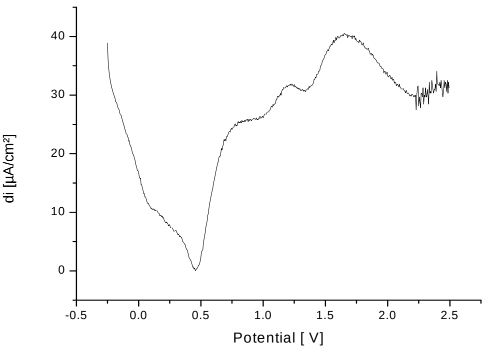
Figure 1. Cyclic voltammograms using platinum wire electrode for (a) 0.1 M KOH and (b) 0.01 M KOH + 0.45 M ethanol. Scan rate: 10 mVs^{-1} and electrode surface area: 1.0 cm^2.

For the second peak (Figure 1b.) there is at the potential of 1100-1600 mV, this peaks represent oxidizing of H_2O with the following reaction:

$$2H_2O \longrightarrow 2OH_{\cdot} + 2H^+ + 2e^- \quad E^o = 1{,}470\ V\ (SCE)$$



(a)

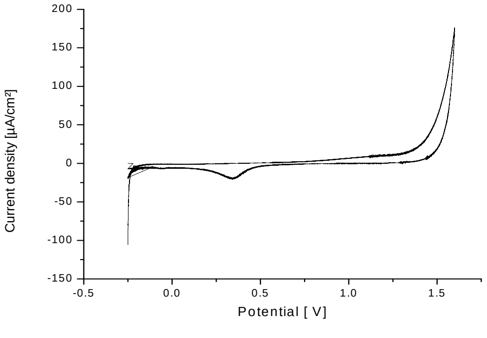


(b)

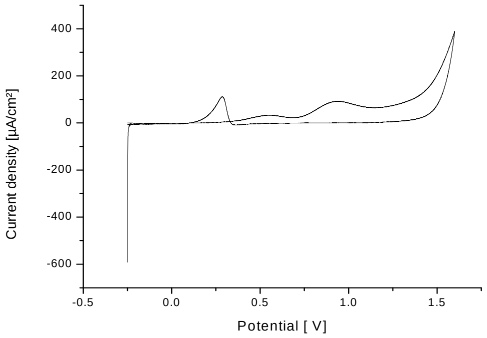
Figure 2. Potential squares curve using platinum wire electrode for (a) 0.1 M KOH and (b) 0.01 M KOH + 0.45 M ethanol. Scan rate: 50 mVs^{-1}. Electrode surface area 1.0 cm^2.

Oxidation process has to be ascertained to happen for ethanol, this matter is conducted by special CV for electrolyte (0.1 M KOH) as seen in Fig. 1a. The Fig 1a shows that there is no peaks that can be observed at 600-1065 mV of current density. The above data can be used for the electrolysis with Chrono Coulometry (CC) to found out the oxidation product of ethanol which was carried out at 600-1065 mV. To support cyclic voltammograms, potential squares curve was needed, because the possibility that there is too low peaks like in CV of ethanol with KOH.

Figure 2b shows that there are three peaks observed at the potential above 500 mV. Peak 1 is at the potential of 600 mV, the second peak is at the potential of 1100 mV and the third peak is at the potential of 1400 mV. These peaks can be seen clearly compared to CV (Figure 1a.), because of the water concentration that is big enough. Potential squares oxidation of ethanol happened at peak 1 and 2 with a potential of around 500-1100 mV. Figure 2a potential squares for KOH showing inexistence culminate at the potential of 500-1100 mV. The matter shown above was happened only to the oxidation of water.



(a)



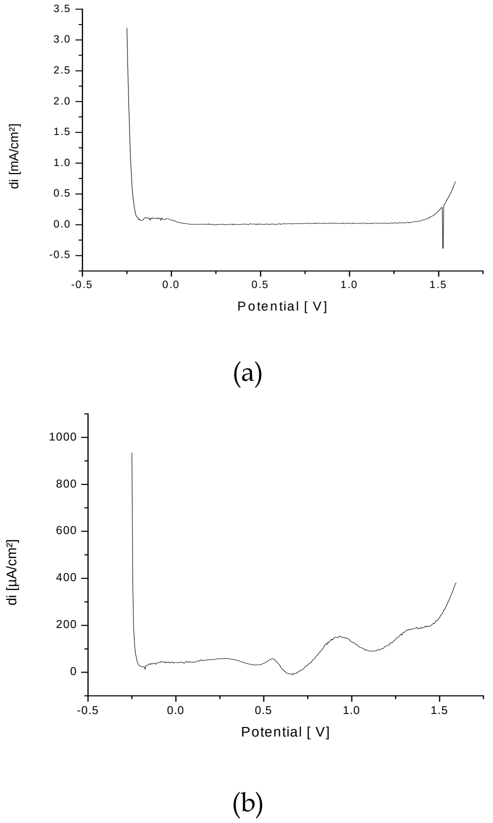
(b)

Figure 3. Cyclic voltammograms using platinum wire electrode for (a) 1.0 M $HClO_4$ and (b) 0.1 M $HClO_4$ + 0.45 M ethanol. Scan rate: 10 mVs^{-1}. Electrode surface area 1.0 cm^2.

3.2 Oxidation of ethanol in acidic medium

Oxidation potential of ethanol in acidic medium is very differ from CV using alkaline medium, but the oxidation potential of ethanol is quite the same with alkaline medium. CV of ethanol in acidic medium can be seen in Figure 3.

Figure 3b shows that there are two peaks which are also designate oxidation of water and ethanol with the same reaction occurred in alkaline medium. First peak is residing at the potential around 700-1125 mV while for the second peak it is residing at bigger potential, 1125 mV. Figure 3a representing the cyclic voltammogram of electrolyte 1.0 M $HClO_4$. There are a few differences between voltammogram obtain in alkaline and acid mediums. Alkaline medium give out a bigger current density compared to acid medium.



(a)

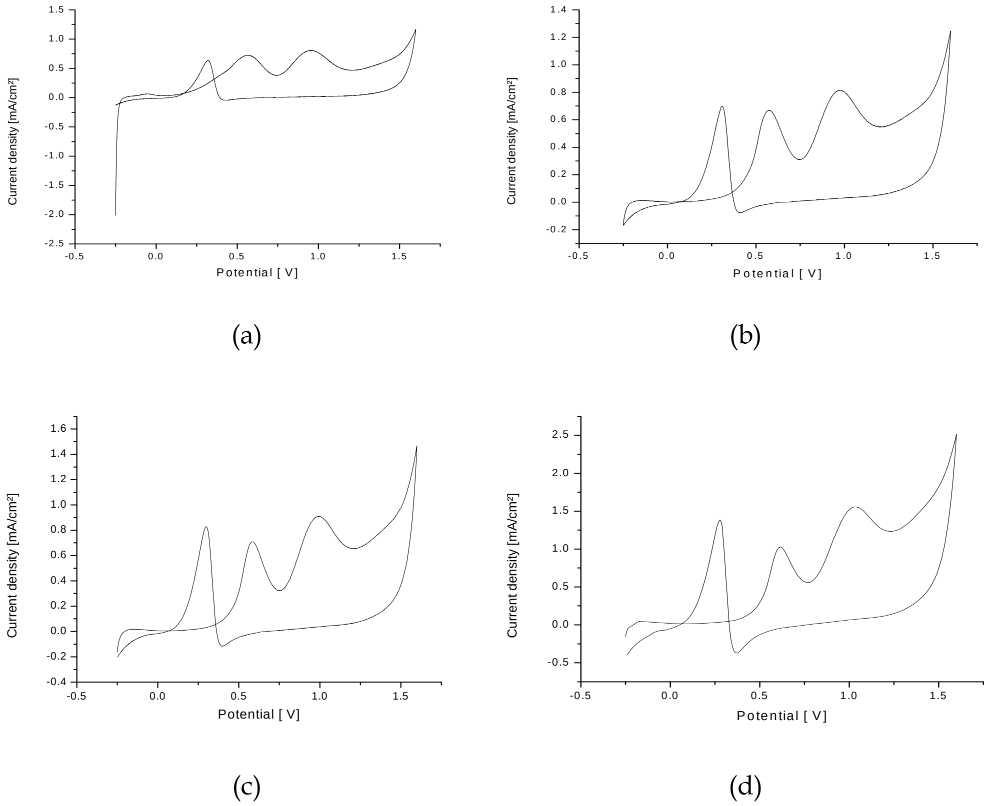
(b)

Figure 4. Potential squares using platinum wire electrode, for (a) 1.0 M $HClO_4$ and (b) 0.1 M $HClO_4$ + 0.45 M ethanol. Scan rate: 50 mVs^{-1}. Electrode surface area 1.0 cm^2.

Low peaks at CV of ethanol in acid make it more complicated to determine the oxidation area. Curve of potential squares can be used to help us determine the oxidation potential of ethanol. Curve of potential squares can be seen in Figure 4. Figure 4a curve of potential squares for $HClO_4$ shows that there are no oxidation peaks observed at the potential between 600-1100 mV. Figure 4b shows that peaks which are equal to CV of ethanol at acid medium occurred at a potential around 700-1125 mV and oxidation of water occurred at a potential of above 1400 mV.

3.3 Scan rate effects

One of the ways to clarify oxidation area can be done by changing the scan rate. Scan rate effect can be seen in Figure 5. Figure 5a-d seen that increasing scan rate culminate and excelsior of current density. Results obtained suggested that bigger scan rate should be used because of its clear peaks and quicker analysis time. In Figure 5 shows that the higher the scan rate is, the bigger the peaks obtained.



(a) (b)

(c) (d)

Figure 5. The effect of scan rate on the cyclic voltammograms of 0.08 M $HClO_4$ + 0.45 M C_2H_5OH using platinum wire as the working electrode. (a) 50 (b) 100 (c) 150 and (d) 250 mVs^{-1} respectively. Electrode surface area 1.0 cm^2.

3.4 Ethanol oxidation products

According to some researchers, the oxidation of ethanol will produced both acetic acid and acetaldehyde as the most probable oxidation products [3,5,6,9,17]. Oxidation products of ethanol depend on some factors such as: the type of the electrode, the electrode area, the concentration of ethanol, the electrolysis time, the pH of the solution, the electrolyte type and last but not least, the voltage. Table 1 shows the percentages of acetic acid produced by the electrochemical oxidation of ethanol in various electrolyte solution obtained in this study.

Table 1. Reaction yields of acetic acid obtained by the HPLC analysis of the electrolysis (E = 1065 mV) experiments using 0.008 M KOH + 0.45 M C_2H_5OH and 0.08 M $HClO_4$ + 0.45 M C_2H_5OH. Electrode surface area 1.0 cm^2

Electrolysis time (minit)	*Supporting electrolyte and reaction yields (acetic acid %)*	
	0.008 M KOH	*0.08 M $HClO_4$*
15	-	-
30	7.83	2.37
120	30.21	8.99
240	49.22	17.24

Table 1 shows that acetic acid forming started when the electrolysis time is 30 minutes. Acetic acid would not be formed if the electrolysis time is fewer than 30 minutes because of phase of adsorption of ethanol on the electrode surface [17] and the volume and the concentration of ethanol which is big enough compared to the electrode surface area. Table 1 also told us that longer period of electrolysis may increase the oxidation product. However, if the electrolysis time was continued much longer, hence ethanol will finish and acetic acid produced will turn into other compound like acetaldehyde. The duration of electrolysis time is really depends on the surface area of the electrode. Alkaline medium is better to produce acetic acid compared to acidic medium due to the mechanism as suggested by Xia, et al., (1997) where OH or known as alkaline medium are needed. To increase the result of acetic acid percentage produced, a longer electrolysis time with wider electrode surface area and other optimum condition had to be applied.

4. CONCLUSIONS

The electrochemical oxidation of ethanol on platinum electrode in 0.008 M KOH and 0.08 M $HClO_4$ was evaluated. The oxidation potential of ethanol in 0.008 M KOH ranges between 600-1065 mV, while the oxidation potential of ethanol in 0.08 M $HClO_4$ ranges from 700-1125 mV. From these cyclic voltammetry experiments, the potential suitable for prolonged electrolyses was at 1065 mV. Scan rates effects on cyclic voltammograms shows that bigger scan rates may increasing the current density. However, it will not affected the oxidation potential of ethanol. According to the HPLC result, electrolysis at longer time, more acetic acid will be formed. Alkaline medium is far better in supporting electrolyte compared to acidic medium to produce acetic acid by electrooxidation process.

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