

SYNTHESIS OF ACETIC ACID FROM ETHANOL BY ELECTROOXIDATION TECHNIQUE USING Ni-Cu-PVC ELECTRODE

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ABSTRACT

A usage of Ni-Cu-PVC electrode for the oxidation of ethanol by electrochemical technique will be reported in this paper. In this work, the effect of electrodes on the yields of acetic acid was determined. Electrode used was made of the mixtures of Ni powder, Cu powder and of polyvinyl chloride (PVC) with various percentages. Electrooxidation of 0.20 M ethanol in 0.16 M KOH (24 mL) were carried out using chrono coulometry (CC) at a potential of 1050 mV for 6 hours with continuous stirring. Electrooxidation result obtained was analyzed using High Performance Liquid Chromatography (HPLC). The test result shows that the composition of Ni:Cu:PVC at 75:20:5 have higher efficiency in the electrooxidation of ethanol to acetic acid.

Keywords: Ethanol, Electrooxidation, Acetic Acid and Ni-Cu-PVC electrode

1. INTRODUCTION

Being as an important industrial chemical, acetic acid was used in the production of polyethylene terephthalate (e.g. for soft drink bottles), cellulose acetate (for photographic film) and vinyl acetate as well as many synthetic fibers and fabrics. Total worldwide production of virgin acetic acid is estimated at 5 Mt/y, approximately half of which is produced in the United States. European production stands at approximately 1 Mt/a and is declining and 0.7 Mt/y in Japan. Another 1.5 Mt are recycled each year bringing the total world market to 6.5 Mt/y [1].

Acetic acid were produced by both synthetically and by bacterial fermentation. Today, the biological route accounts for only about 10% of world production, but it remains important for vinegar production, as in much of the world food purity laws stipulate that vinegar used in foods must be of biological origin. About 75% of acetic acid used in chemical industry was made by methanol carbonylation. Process of methanol carbonylation still being used for the production of acetic acid from methanol [1]. Methanol carbonylation process using ordinary chemistry reaction or organic synthesis conventionally. Process of methanol carbonylation needs high cost raw material like methanol, CO and catalyst. Methanol carbonylation process also need to be carried out high temperature and pressure. This process has many weaknesses, in consequence a production process of acetic acid with electrochemical or more knowledgeable by the name of electrosynthesis technique was proposed.

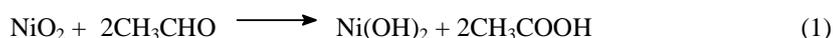
The present works concern the electrosynthesis of acetic acid from ethanol using electrooxidation technique. Recently, a new electrooxidation of ethanol for application in fuel

cells system and study of electrochemical oxidation of ethanol were developed [2 - 7]. Those studies may probably lead to the design of catalyst for an effective oxidation of organic molecules that are being used as a 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 [8, 9].

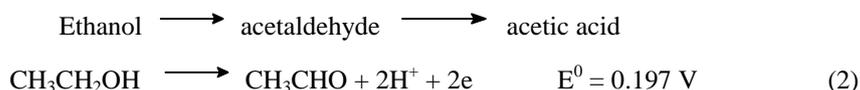
The most important part of any electrosynthesis system is the electrode. Usually, however, it is the working electrode that is of greatest concern. The most prudent way to select an electrode, that is, its material and its surface morphology, is, as a general rule, by direct experiment. Besides chemical and electrochemical stability, electrodes are chosen for industrial use have to be relatively inexpensive, highly conducting, and electrocatalytic [10]. Electrooxidation of ethanol with solid electrodes have many weaknesses especially related to the roughness of electrode, wide of contact with condensation and ability of absorption of condensation. In consequence, development of heavily pressed powder electrode require has to be done, which one of its target is to improve the roughness of electrode.

Among other factors that affected the electrooxidation products is the electrode's surface composition (the variability on the particles size either supported and non-supported) and supporting electrolyte. By using Cu powder with PVC as supported medium, it was expected that particles size can be improve. Usage a nickel mixture with Cu expected could improve the nature. Nickel has been used as an electrodes by many researches for the electrooxidation of ethanol. Nickel for the oxidation of primary alcohol could yield carboxylic acid [11]. Nickel to form electrode into Cu-PVC or has been known as a nanoparticle electrode of. Nickel represent electrocatalytic which is good to yield acetic acid [12].

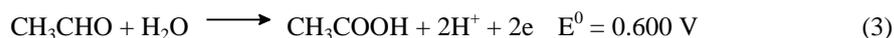
Nickel can alter acetaldehyde to become acetic acid with the following reaction [12]:



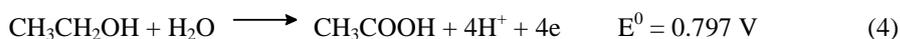
Acetaldehyde represents the oxidation product of ethanol at low potential or start of electrolysis which is as follows [13]:



Acetaldehyde later will be converted to become acid acetic.



The whole oxidation process that occurred at anode is:



For the optimization work, the most essential parameter is the selection of an electrode (anode) material, where an anode material should exhibit good electrochemical efficiency, stable in supporting electrolyte used and commercially available. Among these metal, nickel, copper and raney-nickel are highly tested and the cheapest but show low stability because of their high corrosive properties. The weakness of making an electrode with electrodeposition process is Cu was closed to Ni so that the nature of electrocatalytic of Cu will lose. In consequence it is propose that a new electrode design by directly mingling between nickel powder and copper powder with certain portion, where PVC and tetrahydrofuran (THF) as a solvent were used to strengthen the bonding. This in house design electrode is expected can be exploited the nature of catalytic from both metals nickel of copper.

2. EXPERIMENTAL

2.1 Solution

All solutions were prepared by dissolving its analytical grade salt in deionised distilled water. KOH (R & M Chemicals) was used as the supporting electrolyte. Nitrogen gas was used to deaerate the solutions for 10 minutes to keep an inert atmosphere over the solution. Ethanol solutions were prepared by dilution of absolute ethanol (BDH laboratory) with deionised water.

2.2. Preparation of electrodes

NiCu-PVC electrode was made by mixing together Cu powder (100 mesh 99.9%, System), Ni powder (100 mesh 99.9%, Aldrich Chemical Company) and PVC at a certain portion, 4 mL tetrahydrofuran (THF) was later added and swirled. The mixture were later drying in an oven at 50°C for 3 hours. Homogenous powder was later pressed at 10 ton/cm².

2.3. Analysis electrooxidation product

Analyses were carried out using the High Performance Liquid Chromatography (HPLC) equipment comprised of a pump (Waters 1515 Isocratic HPLC Pump), a column (C18) and two detectors which are an UV-visible detector (Waters 2487, Dual 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% H₃PO₄ was applied.

2.4. Electrochemical measurements (cyclic voltammetry and chrono coulometry)

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

2.5. Experiment procedure

The electrolysis process was performed on a solution of 0.25 M ethanol in 1.0 M and 0.1 M KOH at room temperature. The electrochemical studies by cyclic voltammetry (CV) and oxidation of ethanol by potentiostatic method chrono coulometry (CC) were performed in a glass electrochemical cell (volume 25 mL) with a platinum plat as a counter and NiCu-PVC as working electrodes. The potential of the working electrodes was measured against a SCE reference electrode. Electrolysis products were analyzed by the High Performance Liquid Chromatography (HPLC).

3. RESULTS AND DISCUSSION

3.1 Physical characterizations of the electrode

Figure 1a shows that made electrode by including Cu powder and Ni powder into PVC will yield a scraggly surface. Existence of white colours show PVC, black is Ni metal and red is Cu metal. This may cause the crudity of the electrode surface. The weaknesses of electrode design like this is the metal concentration on the electrode surface do not uniform, so that its ability

may reduce.. After using, NiCu-PVC electrode will give a green colour on the surface, because Ni will be oxidized to form Ni(OH)₂.

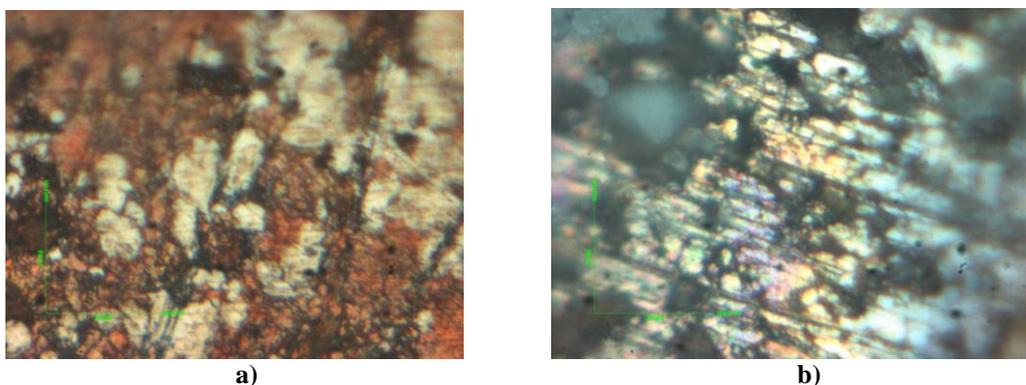


Fig. 1: Image analyser picture of a) NiCu-PVC electrode originally and b) NiCu-PVC electrode after used.

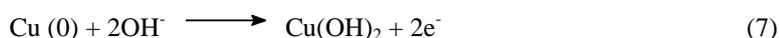
3.2. Voltammetric response using cyclic voltammetry

At Fig. 2. cyclic voltammograms sweep from a potential of -700 mV to 700 mV and back to the starting potential. A1, A2, A3 and A4 represents the peaks obtained on the anodic scan or anodic peaks. This peaks due to the oxidation Cu. Cu metal is easy to oxidize to form its oxide compound. In alkaline medium, it will form a thin coating on the surface of the electrode Cu₂O, CuO, and Cu(OH)₂, besides other species, are deposited on the electrode surface depending on the potential, pH, the mass-transport conditions and ageing and surface restructuring processes [14].

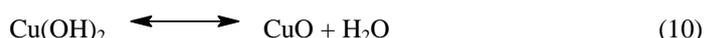
Peak at -400 mV (A1 peak), represent the oxidation Cu (0) or Cu metal to become Cu (I) that is in the form of CuOH and Cu₂O. Cu₂O represent the intermediate layer [15, 16]:



The biggest and highest peak of A2 represent the oxidation of Cu(0) becoming Cu (II) and Cu (I) become Cu (II), with the following reaction:



Reaction of oxidation also come from Cu₂O represent layer which there are on the surface of electrode.



The anodic peak (A3) which represent the oxidation of Ni (II) to Ni (III) happened at maximum potential 320 mV (Fig. 2a). The thin layer of Ni(OH)₂ on the surface of nickel electrode reacted with OH⁻ and forming NiOOH that will adsorbs ethanol on the surface of the electrode. NiOOH was unctioning as catalyst to form intermediates. OH⁻ species coming from KOH or water has an important role. In consequence electrolyte concentration (KOH) has an big effect on in the

electrooxidation of ethanol to acid acetic. Reaction mechanism that occurred on the electrode surface can be seen from formed of spongy on the electrode surface (Fig. 3).

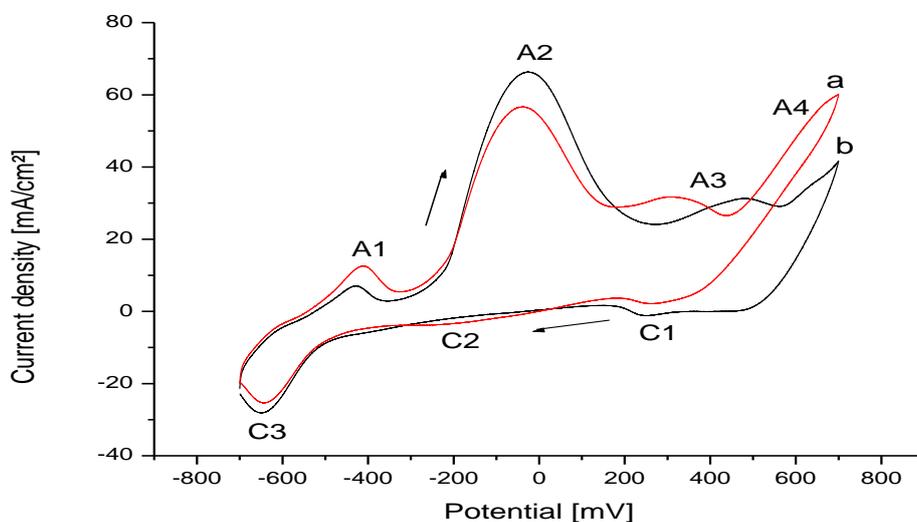


Fig. 2: Cyclic voltammograms of NiCu-PVC electrodes in a) 0.20 M ethanol + 0.8 M KOH and b) 0.8 M KOH + 20 mL water (without ethanol). Scan rate 10 mV/Sec.



Fig. 3: Spongy at NiCu-PVC electrodes, the electrolysis $E = 1050$ mV experiments using 0.2 M C_2H_5OH , 0.16 M KOH, electrolysis time 6 hours at room temperature.

There are spongy with four different colours black, blue, green and gray (Fig. 3). Black colour may represent of CuO compound (reaction 8 and 10) and NiOOH, green colour represent Ni(OH)₂ and Cu₂O₃ compound, blue colour is the Cu(OH)₂ compound while gray colour compound not yet been determined. The forming of the compound only observed for electrolysis at high concentration of KOH. With longer electrolysis times more and more spongy will be formed, the compounds are hard and very stable. The peak of A3 which

represent the oxidation of Ni (II) to Ni (III) can be seen by Cu-PVC cyclic voltammograms (Fig. 4). At Fig. 4 there is no A3 peak (at 320 mV), because there are no nickel in the Cu-PVC.

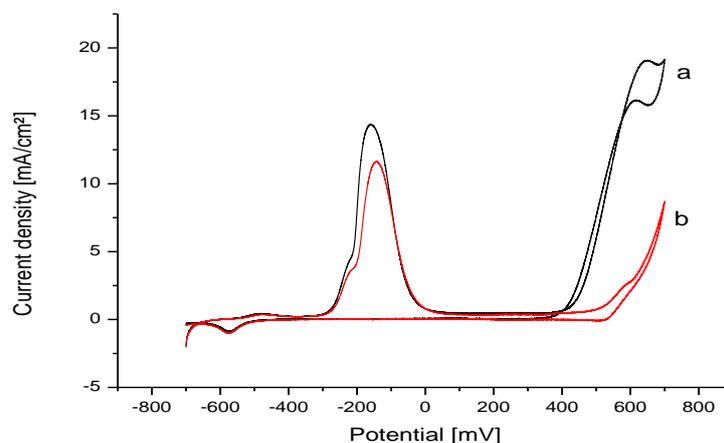
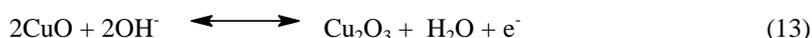
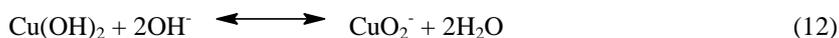
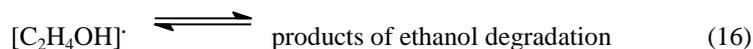


Fig. 4: Cyclic voltammograms of a) 0.2 M ethanol 20 mL in 0.8 M KOH and b) in 0.8 M KOH using Cu-PVC electrodes. Scan rate 10 mV/Sec.

Results to identify this were done by Libria and Pereira [12, 17]. Peak of A4 represent furthermore oxidation peak of Cu become Cu (III). Cu (III) species are more easily to be formed, and indeed detected at high hydroxide concentration by the reaction below [15]:



Cu (III) was detected at a potential 0.6 V during the positive scan. The formation of Cu (III) species at $E > 0.6$ V may have a similar role in the electro catalytic process. Mechanism of electro catalytic that happened at ethanol electro oxidation is [12]:



Electrode designed in this study was different compared to by Periera et al. ¹². In this study, both metal, Ni and Cu able to share as an electrocatalytic. During the electrolysis, electrode surface will form NiOOH, CuO and Cu₂O compounds which were able to act as a catalyst so the weakness of electrode designed by Periera et al. ¹² could be overcome. In the electrode designed by Periera et al. ¹², Ni will be deposited on Cu during the process of electrodeposition, so Cu surface will be not contacted with reactant resulting that Cu cannot act as an electrocatalyst.

C1, C2 and C3 peaks represent cathode peaks which is scan from 700 mV to -700 mV. C1 peak represents reduction of Ni (III) to Ni (II) at potential of 250 mV. C2 peak represents reduction of Cu (III) to Cu (II) and of C3 at potential -650 mV represent reduction peak of Cu (II) to Cu (I) and Cu (I) to Cu (0).

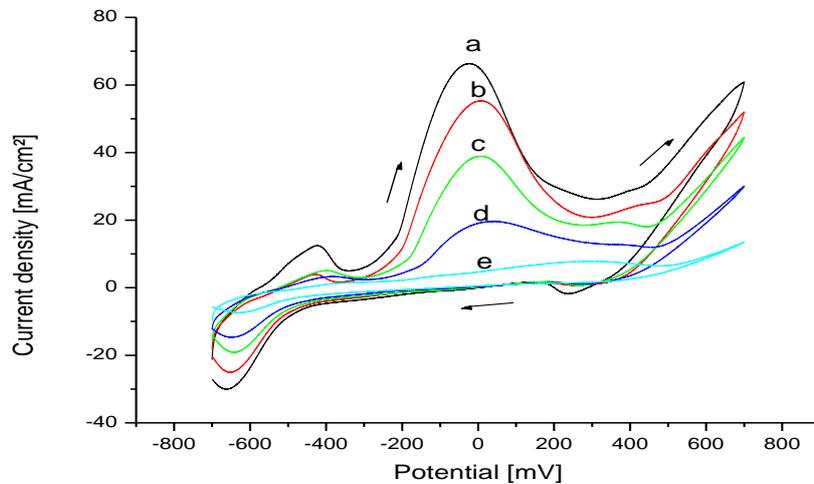


Fig. 5: Cyclic voltammograms of NiCu-PVC electrodes in 0.20 M ethanol + KOH: a) 0.8 M b) 0.6 M c) 0.4 M d) 0.2 M and e) 0.1 M. Scan rate 10 mV/Sec.

At Fig. 5, greater concentration of KOH hence increase the current density, good to peak at 0 mV (peak A2 at Fig. 2) and also peak at 600 mV. Invisible peak progressively at concentration of KOH under 0.5 M, no current peaks were observed in the positive potential range when cyclic voltammograms were recorded with the copper electrodes at supporting electrolyte concentrations lower than 0.1 M NaOH [14]. The rate of an electrochemical process is expressed by the current density that is the current flow per unit area. Lower current density would signify very low rates of conversion of reactant.

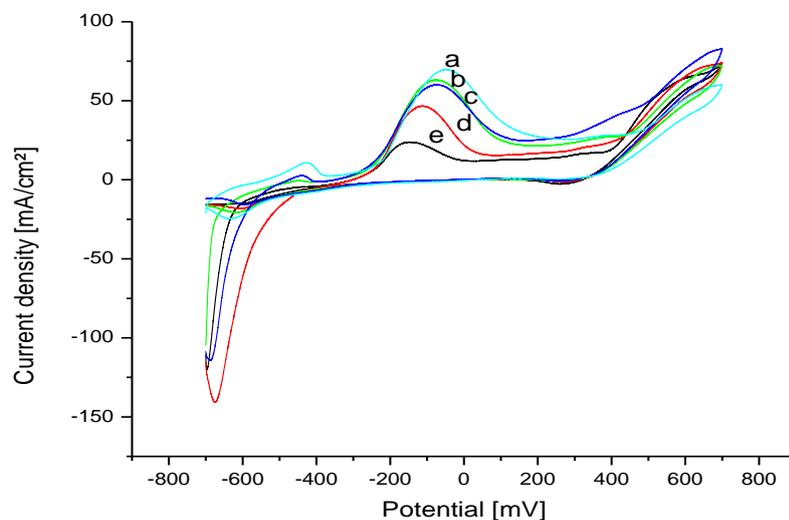


Fig. 6: Cyclic voltammograms in 0.20 M ethanol + 0.16 M KOH using NiCu-PVC electrodes by various comparison Ni:Cu:PVC is; a) 45:50:5 b) 55:40:5 c) 65:30:5 d) 75:20:5 and e) 85:10:5.

Figure 6 shows that are greater concentration of nickel, current density decreased, conversely concentration of copper current density increased. Both of this metal is expected to give the nature of catalytic which is better compared to Cu-PVC and Ni-PVC electrode. If the

composition of Cu is lower in the electrode, hence lower peak height. Meanwhile Ni peak also experience of degradation but did not as much as Cu. At higher KOH concentration, Cu will be more easily to oxidize compared with Ni.

3.3. Analysis of electrooxidation products

Table 1: Reaction yields of acetic acid obtained by the HPLC analysis of the electrolysis $E = 1050$ mV experiments using 0.20 M C_2H_5OH , 0.16 M KOH, electrolysis time 6 hours at room temperature. Electrode surface area 1.0 cm^2

Type Electrodes (Anode)	Conversion to Acetic acid (%)	Current Density (mA/cm^2)	Current Efficiency (%)
NiCu-PVC (45:50:5)	16	16.79	41.36
NiCu-PVC (55:40:5)	20	20.91	49.44
NiCu-PVC (65:30:5)	29	30.87	93.54
NiCu-PVC (75:20:5)	39	41.47	95.33

Table 1 shows that the electrolysis of 0.20 M ethanol in 0.16 M KOH electrolyte give of better result if electrode with higher composition of nickel was used, due to higher concentration electrolyte were very good to nickel. At higher supporting electrolyte concentration (0.16 M KOH) Cu will be easily oxidized to forms Cu^{2+} (at anode) while at cathode (Pt electrode), Cu^{2+} will be reduced back to Cu. This event can be seen from the deposition of Cu on the cathode surface hence a smaller current density and of current efficiency were recorded (Table 1). At higher composition of Cu, cathode (Pt) will stop functioning for electrolysis especially with higher electrolysis time due to electrodeposition of Cu on Pt electrode (cathode) surface .

4. CONCLUSION

NiCu-PVC electrode has good ability to oxidize ethanol to acid acetic. Ability of NiCu-PVC electrode were determined by comparison of both of nickel and copper metal. NiCu-PVC electrode with the higher composition of nickel will give a better results compare to Cu.

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