Characterization of Ni-Co-PVC and Ni-Cu-PVC Alloys Prepared By Mechanical Alloying Technique (MAT)

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Abstract: A study was carried out to characterize Ni-Co-PVC and Ni-Cu-PVC composite materials prepared by mechanical alloying technique (MAT) using SEM, EDS and electrochemical test. Composite materials were prepared by mixing together 95% of metal powder (Ni+Co or Ni+Cu) with 5% PVC. PVC was used as a binder and tetrahydrofuran (THF) was used as a solvent in composite material preparation. Based on the SEM and EDS studies on those composite materials, both Ni-Co-PVC and Ni-Cu-PVC composite materials were found to be homogeneous and composed of aggregation of nickel and Co particles separated by gaps of PVC. The electrochemical test found that the response is very good in KOH and ethanol solution. Based on the CV, Ni-Co-PVC and Ni-Cu-PVC composite materials showed a synergistic effect as the electrocatalyst. Applications of these materials are as an electrode for electrocatalyst in fuel cell and for electrosynthesis of organic compounds.

Keywords: Ni-Co-PVC, Ni-Cu-PVC, MAT.

1. INTRODUCTION

Electrocatalytic activity of copper and nickel materials was strongly dependent on their morphology, composition, surface area and structure, which in turn depends on the preparation methods [1]. One of the techniques of making the porous electrode is by incorporating polymer material like polyvinyl chloride (PVC) with the powder of respected metals [2-6]. As being the transition elements, with their electronic layer *d* incomplete, these metals have shown good electrocatalytic properties for the oxygen reduction reaction (ORR) and electrooxidation of organic compounds in alkaline solution. Recently, there has been a proposal of copper combined with Pd, Ag, Ni or Au for the ORR [7].

Mechanical Alloying Technique (MAT) is an alternative process used to prepare electrocatalysts. MAT is an intensive energy process of mechanical grinding for the preparation of alloyed powders or composites in powder form. The MAT to prepare cobalt–nickel alloys and to evaluate their performance for the oxygen reduction reaction in alkaline media has been carried out [7]. The higher current density associated to the cobalt–nickel an alloy was attributed to a synergistic effect for the electrocatalytic activity [7]. The existence of the two metals will cause synergistic effect [3,8-10], bifunctional oxygen electrode [11], and active bifunctional catalyst in alkaline solution and improvement in acetic acid formation [12-14]. The addition of certain percentage of Co powder into nickel composite electrode will enhance the electrode reactivity [13-15], increase the oxygen evolution reaction (OER) and will be economically feasible for the commercial use [15].

Powders of nickel and copper metal are widely used in numerous applications because they possess good catalytic, electronic and magnetic properties [8]. Ni powder, for example, has been used in catalysis for the direct cracking of methane whereas CeO_2-supported copper catalysts have been tested for CO reduction. The influences of aggregation on the magnetic properties of Ni nanoparticles synthesized by hydrogen reduction and the magneto-resistance of Ni-based thick films have also been investigated. Nickel and copper powders are extensively used as the active anode material in solid oxide fuel cells. When a metal is associated with another metal in bimetallic or alloy form, the properties of the resulting material can be enhanced with respect to those of the pure metals. This is the case for Ni-based bimetallic particles containing copper, which exhibit better catalytic activity [16,17] and selectivity [18,19] than monometallic nickel [8]. To improve the properties of pure Ni and Cu powders, several methods have been proposed for the preparation of bimetallic and alloyed Ni–Cu particles. Reduction of a mixture of nickel and copper compounds under hydrogen has been used to prepare Ni–Cu–Al and Ni–Cu/Al_2O_3 catalysts, and Ni–Cu alloys. Evaporation of a Ni–Cu alloy and co-condensation with organic solvents gives bimetallic Ni–Cu colloids [20].

Compared with nickel, copper shows lower overvoltage and higher enthalpy of OH^- absorption for the OER [16]. Thus, pure copper can be a good electrocatalyst for the OER. It indicates that the addition of copper with cobalt and nickel would increase the electrocatalytic activity for OER. Although, the oxygen evolution study has been carried out recently using Co-Cu alloy and Ni-Cu alloy, the same by using the prepared Ni-Cu-PVC with mechanical alloy is unknown. Because of the high availability and low cost of copper, the Cu-based anodes will be highly encouraging [21].

In this study, we are concerned with the characterization of Ni-Co-PVC and Ni-Cu-PVC composite material prepared

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by mechanical alloying. These techniques are very simple, using low temperature process, low cost design and the properties of the metal will not change. Scanning electron microscopy (SEM) images show the porous microstructure of the composite material on material surface. Energy dispersive spectroscopy (EDS) or energy dispersive analysis of X-ray (EDX) analysis showed the composition and distribution of Ni and Co on material surface. The electrochemical properties of the composite material were studied by cyclic voltammetry (CV) method in KOH and ethanol solutions.

2. MATERIALS AND METHODOLOGY

2.1. Materials

All solutions were prepared by dissolving their analytical grade reagent (Merck) in deionised distilled water. KOH was used as the supporting electrolyte. Nitrogen was used to deaerate the solutions and to keep an inert atmosphere over the reaction solution during the oxidation process. Ethanol solutions were prepared by dilution of absolute ethanol (BDH laboratory supplies) with deionised distilled water.

2.2. Methodology

Synthesis

Ni-Co-PVC and Ni-Cu-PVC materials were prepared by mixing same weighed portion of Cu powder or Co powder (< 2 micron in size and 99.9% purity, Systerm), Ni powder (< 2 micron in size and 99.9% purity, Aldrich Chemical Company) and PVC in 4 mL tetrahydrofuran (THF) solvent and swirled flatly to homogeneous followed by drying in an oven at 100 ^{o}C for 3 hours. The mixture was placed in 1 cm diameter stainless steel mould and pressed at 10 ton/cm^2. A typical pellet contained approximately same amount of Ni:Co powder and Ni-Cu powder, and approximately 5% of PVC polymer. The total weighed of the pellet obtained is approximately 1.5 g.

Characterization

The surface characterizations of the material using SEM and EDS or EDX were performed on the JSM 5400 microscope equipped with a microprobe Voyager Noran System. Au metal was used for sputtering process.

Electrochemical Tests

Universal Pulsa Dynamic EIS, Voltammetry, Voltalab potentiostat (Model PGZ 402) was used for electrochemical behavior measurement; data acquisition was accomplished using the Voltamaster 4 software. Cyclic voltammetry experiments were performed in a three electrodes system using Ni-Co-PVC and Ni-Cu-PVC pellets as a working electrode (anode), saturated calomel electrode (SCE) as reference electrode and platinum wire as the counter electrode. All potentials given are with respect to the SCE reference electrode.

3. RESULT AND DISSCUSION

3.1. Characterization of Ni-Co-PVC and Ni-Cu-PVC Materials

Fig. (**1A**) shows the SEM micrograph obtained from the morphological study of freshly prepared $Ni_{47.5}Co_{47.5}$-PVC_5 electrode, while Fig. (**1B**) shows the EDS spectrum for the same electrode. The SEM micrograph obtained shows that the electrode surface was very rough, irregular and having porous characteristic (Fig. **1A**). It has been reported that electrode prepared using metal-PVC powder produced an electrode with a very rough surface, irregular and formed a lamellar orientated particles [4-6]. Fig. (**1A**) indicates that the surface morphology is highly homogeneous and composed of aggregates of nickel and Co particles separated by gaps of PVC which voids between aggregate of nickel and cobalt. These morphological, structure and porosity characteristics enable the use of this Ni-Co-PVC composite electrode as current collector for different catalysts with good adherence [4,5]. Fig. (**2A**) shows the SEM micrograph ob-

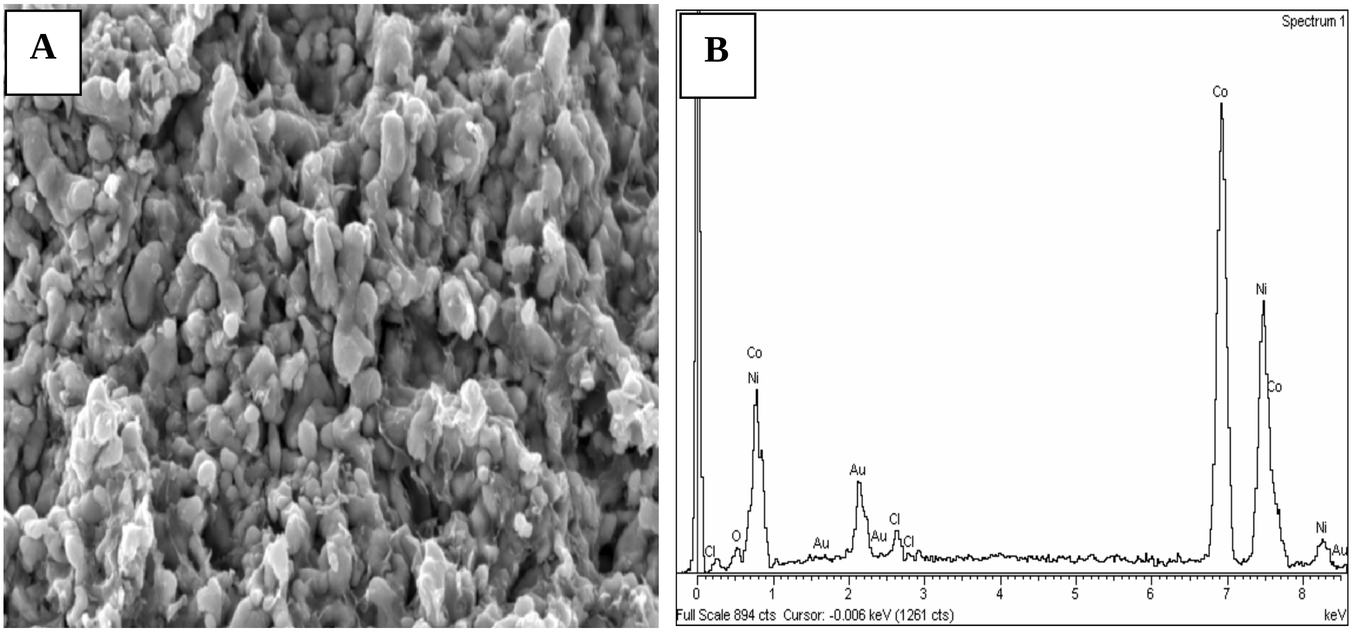

Fig. (1). Physical characterization of $Ni_{47.5}Co_{47.5}$-PVC_5 materials (**A**) scanning electron microscopic images (magnification x4000) at cross section and (**B**) EDS spectra composition analysis.

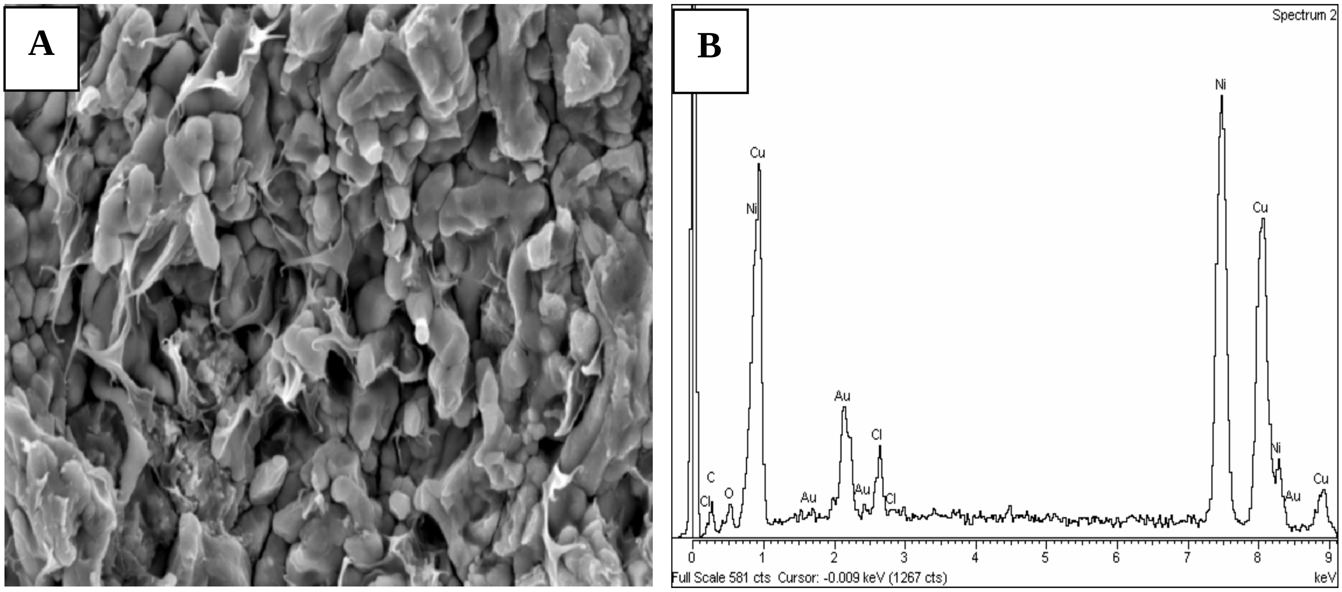

Fig. (2). Physical characterization of $Ni_{47.5}Cu_{47.5}$-PVC_5 materials (**A**) scanning electron microscopic images (magnification x4000) at cross section and (**B**) EDS spectra composition analysis.

tained from the morphological study of freshly prepared $Ni_{47.5}Cu_{47.5}$-PVC_5 electrode, while Fig. (**2B**) shows the EDS spectrum for the same electrode.

3.2. Electrochemical Characterization

Fig. (**3A**) shows the cyclic voltammogram of $Ni_{95.0}$-PVC_5 (Ni-PVC) electrode. The oxidation peaks for the oxidation of Ni (II) to Ni (III) {$Ni(OH)_2$ to NiOOH} are represented by A1 peak (anodic peak) in Fig. (**3A**). Oxidation of Ni (0) or Ni metal to Ni (II) in the form of $\alpha Ni(OH)_2$ has always occurred in the negative potential (-0.8 V up to -1.5 V) (not shown in this cyclic voltammogram) as already suggested by many researches [3,22,23]. While at the potential of -0.8 V up to + 0.3 V, represents the changing process of $\alpha Ni(OH)_2$ to $\beta Ni(OH)_2$, where $\alpha Ni(OH)_2$ was easily change to $\beta Ni(OH)_2$. A1 peak represents the oxidation process of $\beta Ni(OH)_2$ to NiOOH [10,24-28].

C1 (cathodic peak) in Fig. (**3A**) represents two forms of crystallographic from oxyhydroxide α and β [22]. Nickel oxyhydroxide (NiOOH) is capable to oxidize a number of functional groups, for example primary alcohols may be oxidized to carboxylic acids. Nickel has been reported to be a good electrode for the oxidation of various organic compounds [22]. A redox couple of nickel, i.e., nickel hydroxide {$Ni(OH)_2$} and nickel oxyhydroxide (NiOOH) was shown to be involved in the oxidation of alcohol at nickel electrode in alkaline media. Fig. (**3B**) shows the cyclic voltammogram of Co-PVC in 1.0 M KOH. A1 peak represents oxidation of Co (I) to Co (II) and A2 peaks represents oxidation of Co (II) to Co (III) [29]. C1 and C2 peaks represent reduction of Co (III) to Co (II) and Co (II) to Co (I), respectively.

Figs. (**3C**) and (**3D**) show a cyclic voltammogram of Ni-Co-PVC electrode in 1.0 M KOH where both A1 and A2 peaks in Figs. (**3C**) and (**3D**) represent the anodic peaks. A1 peaks represent oxidation of Co (II) to Co (III) and A2 peak represents oxidation of Ni (II) to Ni (III). C1 and C2 peaks in Figs. (**3C**) and (**3D**) represent reduction Ni (III) to Ni (II) and Co (III) to Co (II). From Figs. (**3C**) and (**3D**), redox couple occurred was A1/C2 and A2/C1. Fig. (**3D**) supporting the occurrences of redox couple, the higher the composition of Ni powder (up to 76%), the higher the electrochemical activity for redoxs couple A2/C1 or Ni(III)/Ni(II), while the lower the current density for A1/C2 or Co(III) to Co (II) redox couple. Redox couple is a very important parameter for the electrocatalysis in the electrosynthesis of organic material. According to Kim and Park [30], reaction mechanism of electrocatalyst activity on the surface of Ni electrode is as follows:

$$OH^- + Ni(OH)_2 \rightleftharpoons NiOOH + H_2O + e^- \quad (1)$$

$$NiOOH + CH_3CH_2OH \longrightarrow \text{Intermediate 1} + Ni(OH)_2 \quad (2)$$

$$NiOOH + \text{Intermediate 1} \longrightarrow CH_3CHO + Ni(OH)_2 \quad (3)$$

$$NiOOH + CH_3CHO \longrightarrow \text{Intermediate 2} + Ni(OH)_2 \quad (4)$$

$$NiOOH + \text{Intermediate 2} \longrightarrow CH_3COOH + Ni(OH)_2 \quad (5)$$

and on the surface of Co electrode is as follows:

$$Co(OH)_2 + OH^- \rightleftharpoons CoOOH + H_2O + e^- \quad (6)$$

$$CoOOH + CH_3CH_2OH \longrightarrow \text{Intermediate 1} + Co(OH)_2 \quad (7)$$

$$CoOOH + \text{Intermediate 1} \longrightarrow CH_3CHO + Co(OH)_2 \quad (8)$$

$$CoOOH + CH_3CHO \longrightarrow \text{Intermediate 2} + Co(OH)_2 \quad (9)$$

$$CoOOH + \text{Intermediate 2} \longrightarrow CH_3COOH + Co(OH)_2 \quad (10)$$

Reaction mechanisms 1-5 occurred for the $Ni(OH)_2$/NiOOH redox couple, while reaction mechanism 6-10 occurred for the $Co(OH)_2$/CoOOH couple redox.

Fig. (**4A**) shows the cyclic voltammogram (CV) of $Cu_{95.0}$-PVC_5 (Cu-PVC) in 1.0 M KOH with the sweep potential from potential -700 up to +700 mV, and then return from +700 mV up to -700 mV. The A1, A2, A3, and A4 peaks represent the anodic peaks. These peaks are related to the

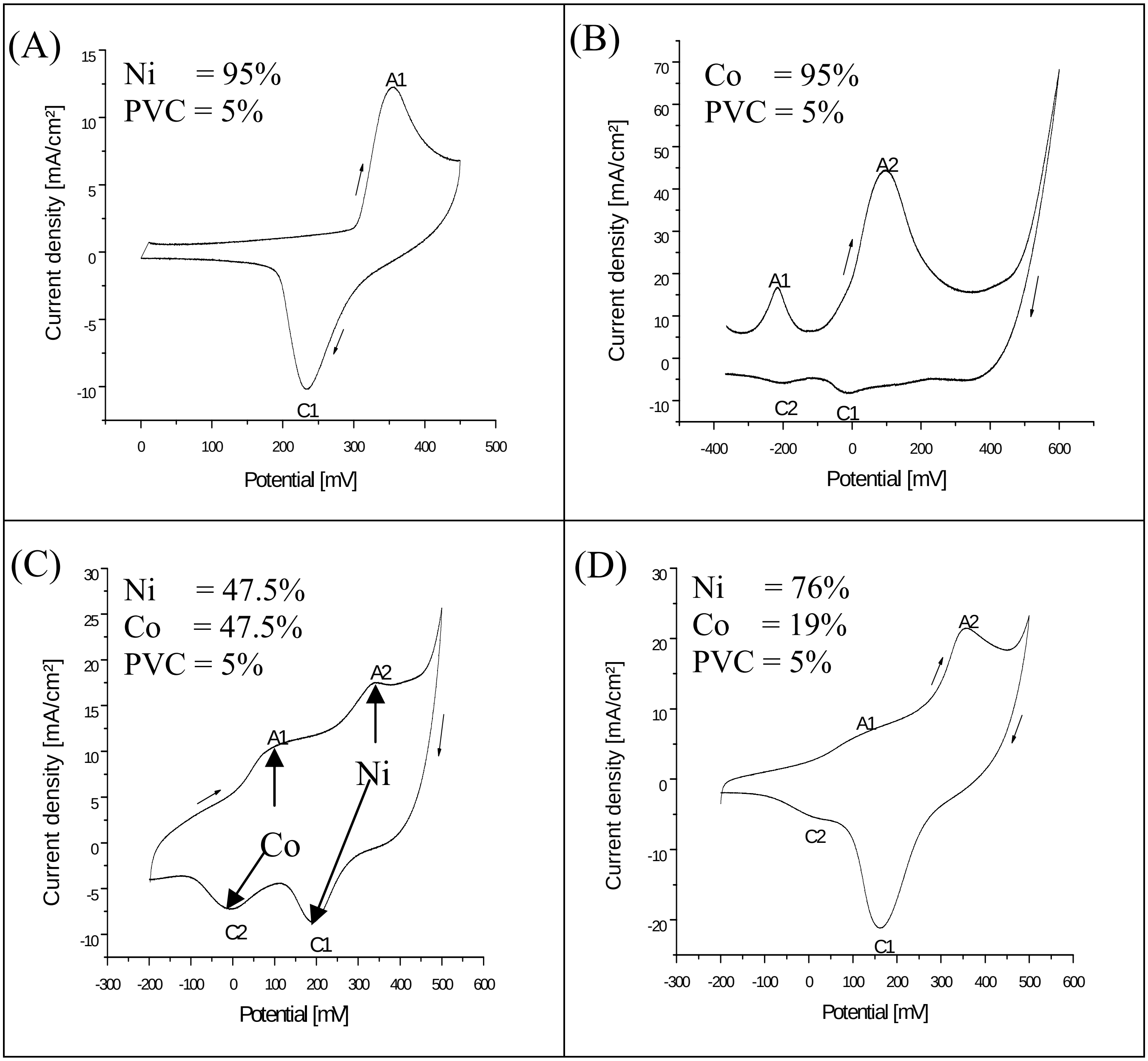

Fig. (3). Cyclic voltammograms in 1.0 M KOH, scan rate 10 mV/sec.

oxidation of Cu to Cu (I), Cu (II) and Cu (III) [2,31,32]. A1 peak represents the oxidation of Cu (0) to Cu (I) {Cu metal to CuOH or Cu_2O} [31,32], while A2 peak represents solubilization of species process [32]. The reaction mechanism of solubilization of species process is as follows [32]:

$$Cu^0 + 3OH^- \longrightarrow HCuO_2^- + H_2O + 2e^- \quad (11)$$

$$Cu(OH)_2 + 2OH^- \rightleftharpoons CuO_2^{2-} + 2H_2O \quad (12)$$

A3 peak represents the oxidation of Cu (I) to Cu (II) and A4 peaks represent the oxidation of Cu (II) to Cu (III) {$Cu(OH)_2$ to CuOOH} [32].

Fig. (**4B**) shows the CV of $Ni_{47.5}Cu_{47.5}$-PVC_5 electrode in 1.0 M KOH indicating that A1, A2, A3 and A4 peaks represent the oxidation of Cu, while A3 peak represents the overlapping oxidation of Cu (I) to Cu (II) and Ni (II) to Ni (III). Mixing of Ni and Cu with the same compositions causing both metals has the same opportunity as electrocatalyst, however the overlapping of the A3 peak will occur. From Fig. (**4B**), the redox couple occurred was A3/C1 and A4/C2 or Ni(III) to Ni (II) and Cu (III) to Cu (II).

3.3. Electrochemical Responds on Ethanol

Fig. (**5**) shows the cyclic voltammograms of 0.25 M ethanol in 1.0 M KOH using Ni-PVC electrode. With ethanol in the reaction mixture (curve a), at 300 mV and below, the oxidation of ethanol is sustained by the involvement of adsorbed hydroxyl group (from KOH) on the electrode surface, while at higher potentials region (300 mV to 500 mV) the electrooxidation process is attributed to the formation of NiOOH species. However, without ethanol (curve b), the adsorption of hydroxyl group (from KOH) and the formation of NiOOH on the electrode surface occurred at higher potential (Fig. **5b**). Adsorption of ethanol on the electrode surface

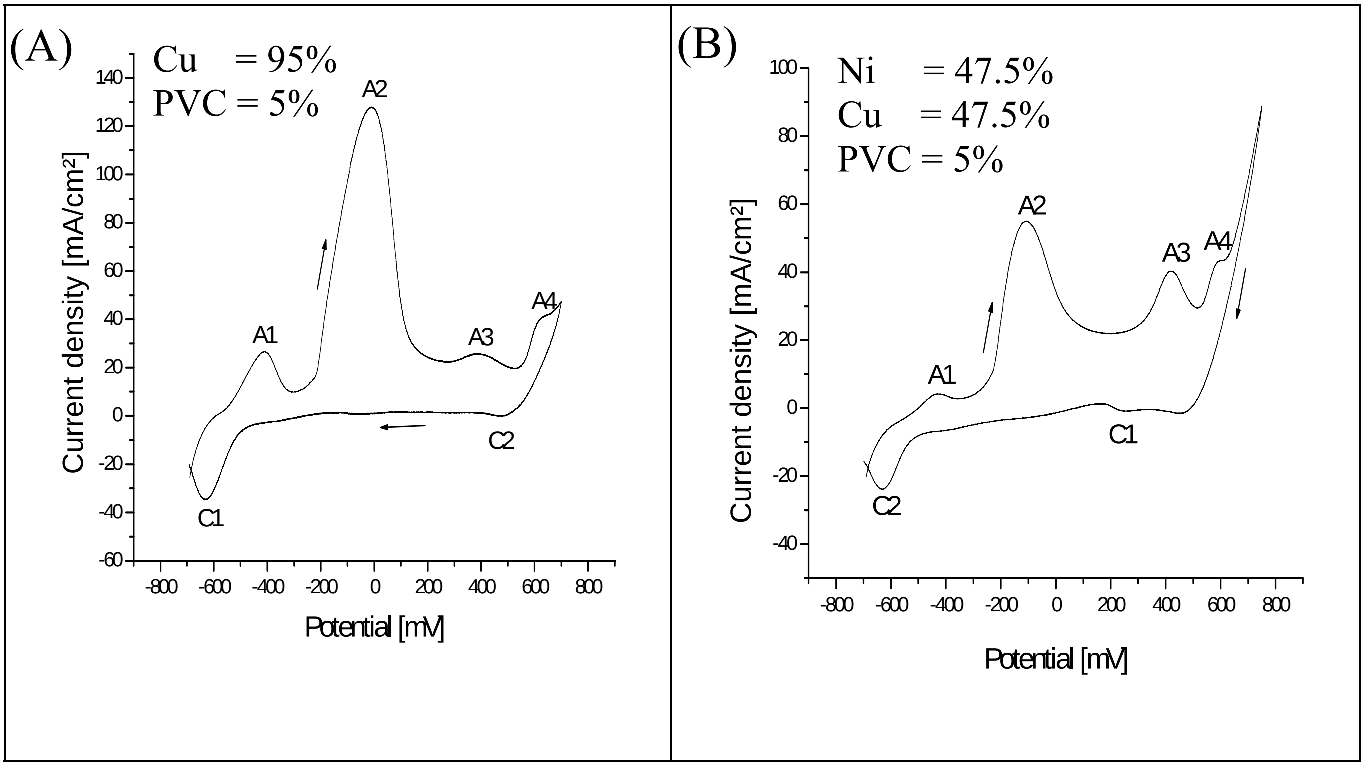

Fig. (4). Cyclic voltammograms in 1.0 M KOH, scan rate 10 mV/sec.

(A2 peak) will immediately occur after the completion of NiOOH formation.

Fig. (**6a**) shows a cyclic voltammogram in 1 M KOH using $Ni_{47.5}Co_{47.5}$-PVC_5 electrode, while Fig. (**5b**) shows the cyclic voltammogram of 0.25 M ethanol in KOH for the same electrode. Peaks A1 and A2 in Fig. (**6b**) represent the oxidation peaks of Co {Co (I) to Co (II) and Co (II) to Co (III)} and A3 peak represents the oxidation peak of ethanol. Electrooxidation of ethanol in alkaline solution may produce acetic acid as yield [33]. Oxidation peaks of Ni (II) to Ni (III) overlap with the oxidation peak of ethanol which was presented by A3 peak. Based on the CV in Figs. (**5**) and (**6**), the $Ni_{47.5}Co_{47.5}$-PVC_5 electrode has shown good activity on electrooxidation of ethanol in alkaline solution compared to Ni-PVC electrode. Oxidation peaks of ethanol using Ni-PVC electrode (A2 peak in Fig. (**5**)) and $Ni_{47.5}Co_{47.5}$-PVC_5 electrode (A3 peak in Fig. (**6**)) showed the current density for both electrodes approximately are 62 $mAcm^{-2}$ and 90 $mAcm^{-2}$, respectively. The higher current density showed higher electrochemical activity [7].

The C1 peak in Fig. (**6a**) is a reduction peak for Ni (III) in the form of NiOOH to Ni (II) which is in the form of $Ni(OH)_2$ [24]. This process is similar to the C1 peak at Fig. (**3A**). According to Hahn *et al.* [26,27] C1 peak which appears in Fig. (**6a**) represents the peak for the formation of β-NiOOH, and the existence of crystallographic form of γ-NiOOH. The α-form is known to be unstable in alkaline solution and slowly converted and irreversible of the β-form, while on prolonged charging; β-NiOOH converts to the γ-oxyhydroxide form [28]. C2 peak at Fig. (**6a**) is a reduction peak for Co (III) in the form of CoOOH to Co (II) which is in the form of $Co(OH)_2$.

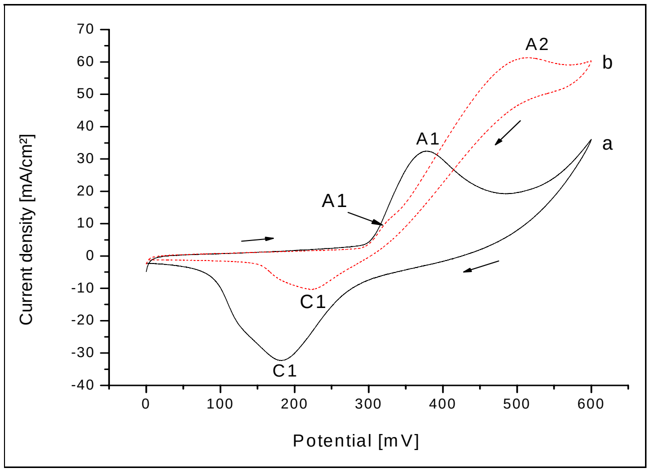

Fig. (5). Cyclic voltammograms of Ni-PVC electrode for (**a**) 1.0 M KOH and (**b**) 0.25 M ethanol in 1.0 M KOH. Scan rate 10 mV/sec.

Fig. (**7a**) shows a cyclic voltammogram of $Ni_{47.5}Cu_{47.5}$-PVC_5 electrode in 1 M KOH while Fig. (**7b**) shows a cyclic voltammogram of 0.25 M ethanol in 1 M KOH with the sweep potential is from -700 mV to +750 mV and returns to the initial potential. A1, A2 and A3 peaks in Fig. (**7b**) representing the anodic peaks from Cu. A4 peak in Figs. (**7a**) and (**7b**) which has a relatively larger anodic current is related to further oxide growth as well as the change in Ni oxidation state from Ni (II) to Ni (III) and possibly higher if overcharging occurs [24].

A4 peak in Fig. (**7a**) representing the oxidation peak for Cu (II) to Cu (III), but with the existence of ethanol, overlapping with ethanol oxidation peak occurred (Fig. **7b**).

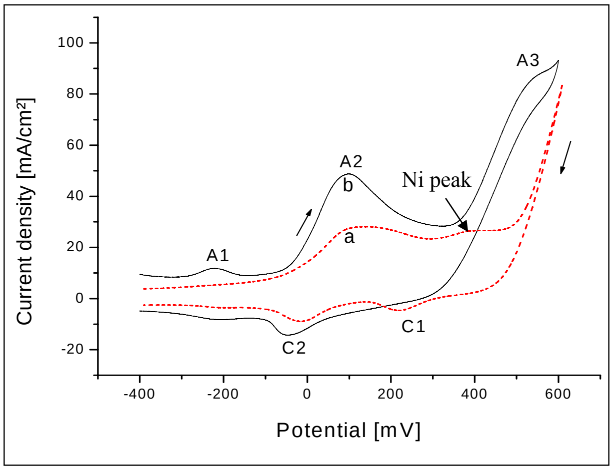

Fig. (6). Cyclic voltammograms of $Ni_{47.5}Co_{47.5}$-PVC_5 electrode for (**a**) 1.0 M KOH and (**b**) 0.25 M ethanol in 1.0 M KOH. Scan rate 10 mV/sec.

From the existing of ethanol oxidation peak, it clearly showed that the oxidation of ethanol with $Ni_{47.5}Cu_{47.5}$-PVC_5 electrode can be done at a potential of 600 mV, where better electrocatalytic reaction would occurr at this potential due to the formation of NiOOH and CuOOH on the surface of electrode used. At potential 600 mV *vs* SCE a synergistic effect electrocatalysts would occur from the NiOOH and CuOOH species.

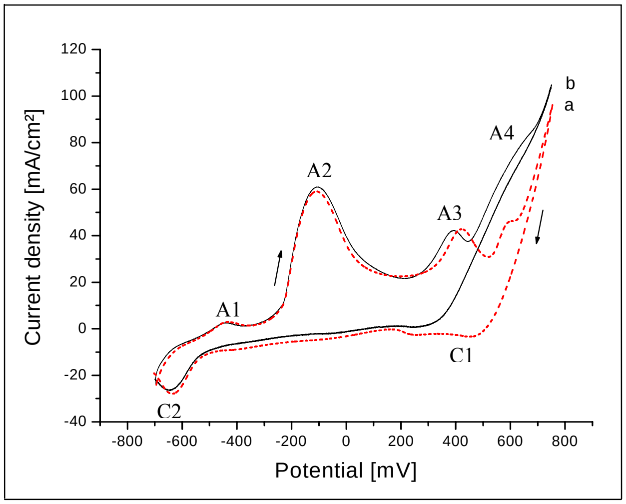

Fig. (7). Cyclic voltammograms of $Ni_{47.5}Cu_{47.5}$-PVC_5 electrode for (**a**) 1.0 M KOH and (**b**) 0.25 M ethanol in 1.0 M KOH. Scan rate 10 mV/sec.

4. CONCLUSION

Mechanical alloying technique was found to be a good technique for the preparation of the composite material. Based on the SEM and EDS studies, both Ni-Co-PVC and Ni-Cu-PVC composite materials were found homogeneous and composed of aggregates of nickel and Co particles separated by gaps of PVC which voids between aggregate of nickel and cobalt. Based on the EDS and CV studies, both metals play the same role on the surface of material so that synergistic effect is easy to occur. The electrocatalytic ability of the composite material towards the oxidation of ethanol in KOH solution was tested and the results indicated that the Ni-Co-PVC and Ni-Cu-PVC composite materials have good electrocatalytic ability.

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