

## Design and Application of Cu, Co, Ni, Pt and Ir Powder Composite Electrode (PCE) For Electrosynthesis and Electroanalysis in Alkaline Solution

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**Abstract:** Design and application of powder composite electrodes for electrosynthesis and electroanalysis research has been carried out. The physical characterization of electrodes was analysis using SEM, EDX and FTIR. The electrochemical stability was analysis using cyclic voltammetry. The stability of electrodes was analyzed using Atomic Absorption Spectroscopy (AAS). The powder composite electrodes were prepared by mixing 95% metal powder with 5% polyvinyl chloride (PVC). PVC was used as a binder and tetrahydrofuran (THF) was used as a mixing solvent in powder composite electrodes preparation. The result, of the study showed powder composite electrode higher stability compared to metal sheet electrode. Electrooxidation of ethanol in KOH solution powder composite electrodes has shown good stability based on analysis using AAS. The composite electrode has shown higher current density, so that we use for electrochemistry research such electrosynthesis, electroanalysis and electrodegradations.

**Keywords:** Electrochemical stability, Composite Electrode, Ethanol, KOH

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### I. Introduction

Electrocatalytic activity of copper and nickel materials strongly depends on their morphology, surface area and structure, composition, which in turn depend on the preparation methods [1]. These metals, being transition elements, with their electronic layer  $d$  incomplete, have shown good electrocatalytic properties for the oxygen reduction reaction (ORR). Recently, there have been proposals of copper combined with Pd, Ag, Ni or Au for the ORR. The mechanical alloying technique to prepare cobalt–nickel alloys and to evaluate their performance for the oxygen reduction reaction in alkaline media has been carried out [2]. The higher current density associated to the cobalt–nickel an alloy was attributed to a synergistic effect for the electrocatalytic activity.

The filling of a polymer with metallic particles results in an increase of both electrical and thermal conductivity of the composite obtained. The influence of the type of polymer matrix and filler on the electrical characteristics of the composite has been studied in many works [3]. One of the techniques of making the porous electrode is by incorporating polymer material like polyvinyl chloride (PVC) with the powder of respected metals [3-8].

Powders of nickel and copper are widely used in numerous applications because they possess good catalytic, electronic and magnetic properties [9]. Ni powder, for example, has been used in catalysis for the direct cracking of methane whereas CeO<sub>2</sub> supported copper catalysts has been tested for NO reduction. The influences of aggregation on the magnetic properties of Ni nano particles 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.

Electrode in electrosynthesis is truly fundamental. According to Couper et al. (1990), some general guidelines to assist the choice of an electrode material are physical stability, chemical stability, suitable physical form, rate and product selectivity, electrical conductivity and cost (lifetime) [10]. The need for a suitable combination of mechanical, physical, and chemical stability has already been stressed. It is important to recognize that the stability must be maintained under all conditions met by the electrode material. Besides chemical and electrochemical stability, electrode are chosen for industrial use to be relatively inexpensive, highly conducting and electrocatalytic. An electrocatalytic electrode is one which exhibits a low overvoltage for a given process. In addition, electrocatalysis implies high product selectivity especially importance in the electrosynthesis of organic compounds.

The present paper aims to describe the electrochemical stability of Cu, Ni, Co, Pt, Ir powder composite electrodes for electrooxidation of ethanol in KOH solution. The electrochemical stability was analysis using cyclic voltammetry. Cyclic voltammetry very suitable for the study of electrochemical stability [11].

## II. Experiments

### Solutions

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.

### Preparation of Composite Electrode

The composite electrode was prepared by mixing a weighed portion of metal 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<sup>o</sup> C for 3 hours. The mixture was placed in 1 cm diameter stainless steel mould and pressed at 10 ton/cm<sup>2</sup>. A typical pellet contained approximately 95% of metal powder and 5% of PVC polymer. The total weighed of pellet obtained is approximately 1.5 g. The same treatments as solid metal foil were later carried out for composite electrode preparation.

### Electrochemical Stability of The Electrodes

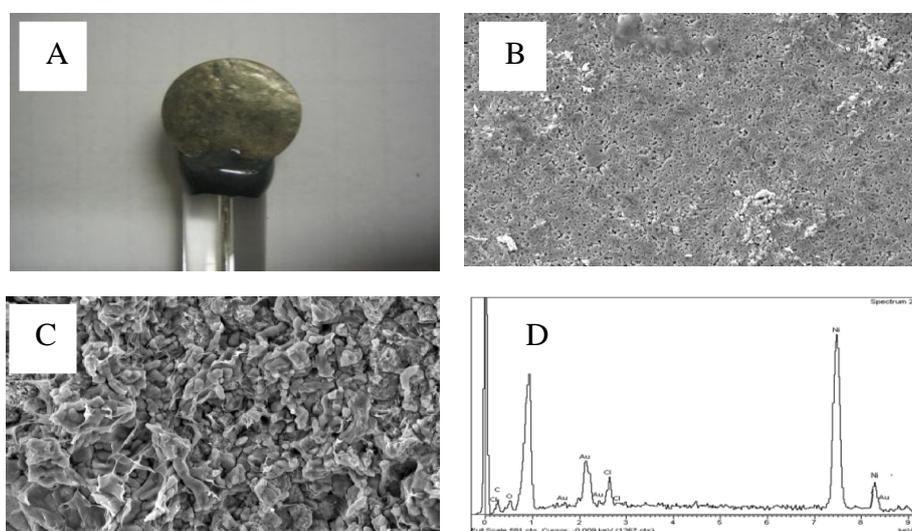
Universal Pula Dynamic EIS, Voltammetry, Voltalab potentiostat (Model PGZ 402) was used for electrochemical stability measurements, data acquisition was accomplished using the Voltmaster 4 software. Cyclic voltammetry experiments were performed in a three electrodes system using composite electrode (Cu-PVC, Ni-PVC, Co-PVC, Pt-PVC and Ir-PVC) as a working electrode (anode), SCE as reference electrode and platinum wire as the counter electrode. All potentials given are with respect to the SCE reference electrode.

### Chemical Stability of The Electrodes

The electrolysis process of ethanol was performed in a solution of 1.0 M KOH at room temperature. The electrochemical stability by cyclic voltammetry (CV) and oxidation of ethanol by potentiostatic (chronocoulometry) method were performed in 25 mL capacity glass electrochemical cell. Chemical stability of the electrode was analyzed using Atomic Absorption Spectroscopy (AAS).

## III. Result And Discussion

SEM micrograph at Fig. 1A shown in electrodes surface were very rough, irregular and having porous characteristic. It has been reported that electrode prepared using powdered metal-PVC yielded electrode have surface which is very rough, irregular, and formed a lamellar orientated particles. The picture shown in Fig. 1B and 1C indicates that the surface and cross section morphology is highly heterogeneous and composed of aggregates of nickel particles separated by gaps of PVC and voids between aggregate of nickel. Analysis on Ni-PVC electrode using EDS showed the existence of Ni, C and of Cl peaks (Fig.1D). The existing C and Cl peaks show the existence of PVC on the surface of the electrode. The bonding between PVC and metal occurred through Cl atom from PVC and metal to form Ni-Cl bonding, which produced a good strength electrode.



**Fig. 1** Electrode Ni-PVC from surface (A) SEM micrograph at surface (B) and cross section (C) with magnification x 1000, and EDS spectra (D).

Fig. 2 showed FTIR spectra of THF+PVC (A) and Cu-PVC electrode. Wavelength number at  $1036.75\text{ cm}^{-1}$  showed C-O bonding, while  $2964.46\text{ cm}^{-1}$  showed C-H bonding. The effect of heated at  $100^\circ\text{C}$  showed new peak at wavelengths number  $2360.41\text{ cm}^{-1}$  and loss of peak at  $2360.41$  and  $3438.28\text{ cm}^{-1}$ .

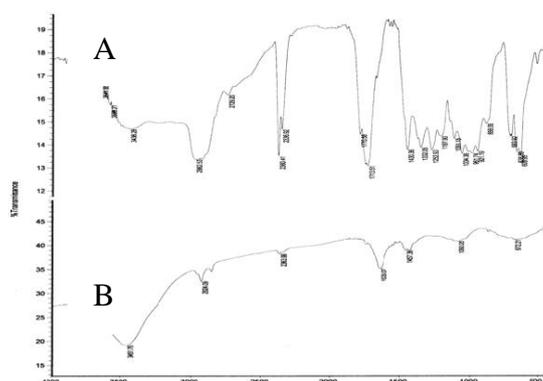


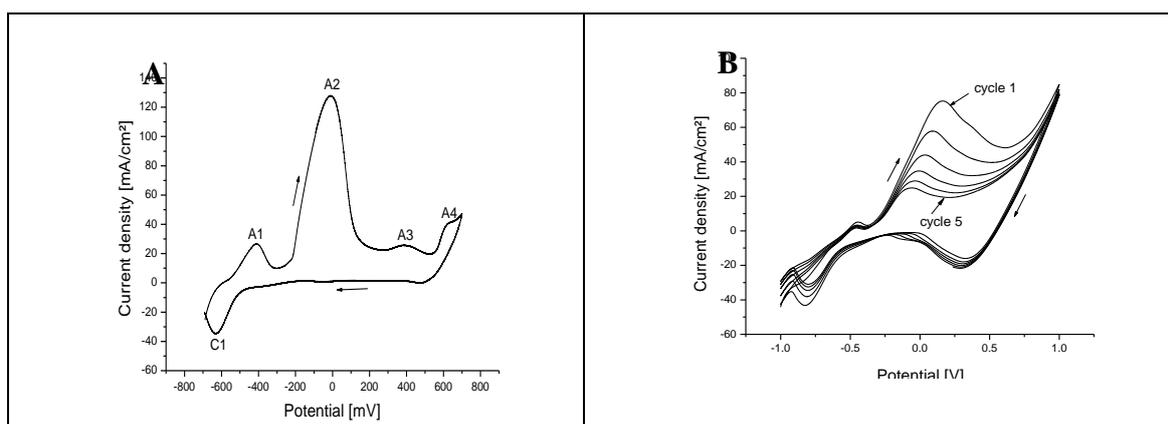
Fig. 2. FTIR spectra of THF+PVC (A) and Cu-PVC electrode (B)

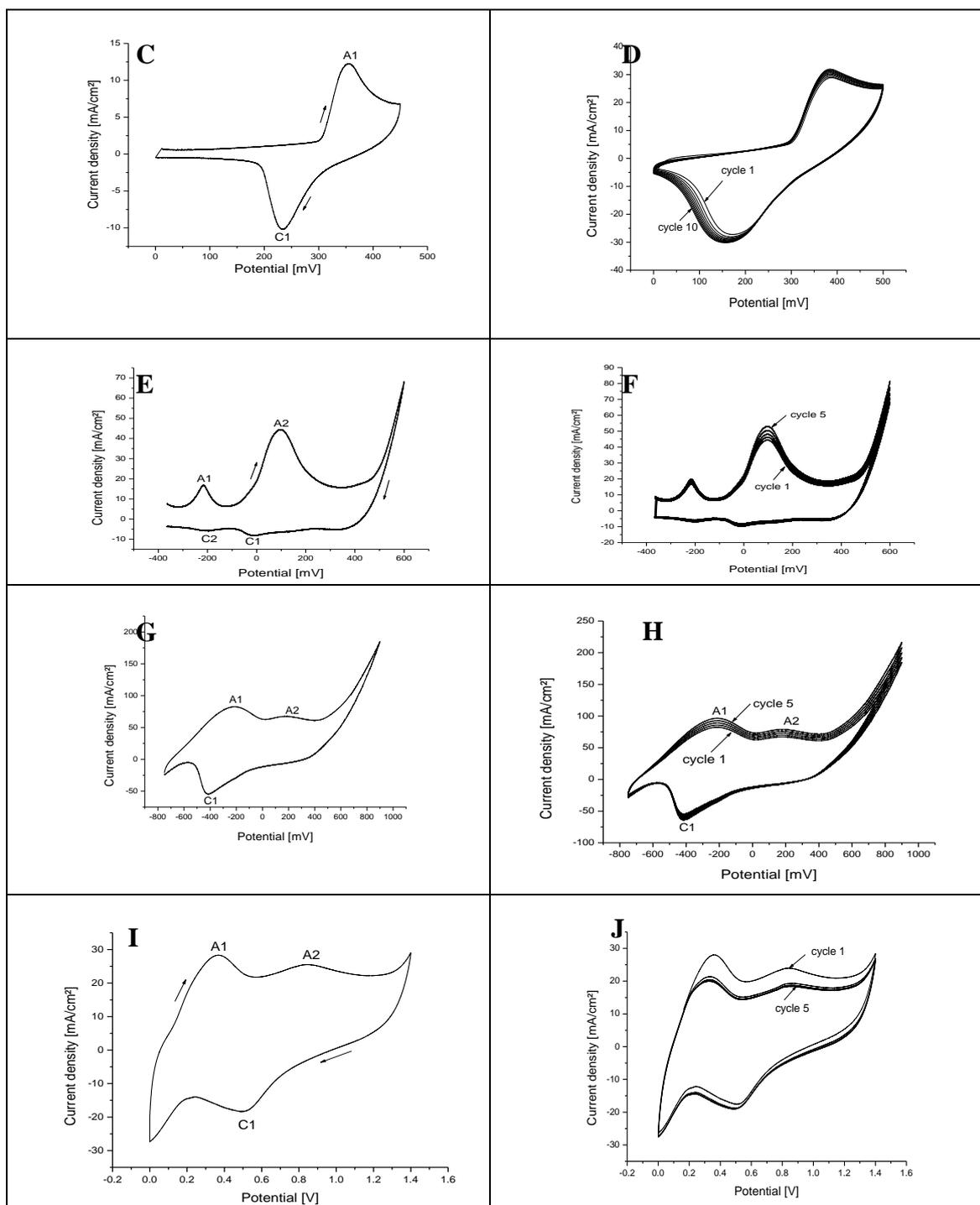
### Cyclic Voltammetry of Composite Electrodes

Fig. 3 (A and B) shows the cyclic voltammogram of  $1.0\text{ M KOH}$  with the sweep potential from potential  $-700$  up to  $+700\text{ mV}$ , and then return from  $+700\text{ mV}$  up to  $-700\text{ mV}$  using Cu-PVC electrode. The A1, A2, A3 and A4 peaks represent the anodic peaks. These peaks related to the oxidation of  $\text{Cu}(0)$  to  $\text{Cu}(\text{I})$ ,  $\text{Cu}(\text{I})$  to  $\text{Cu}(\text{II})$  and  $\text{Cu}(\text{II})$  to  $\text{Cu}(\text{III})$ . The C1 peak in shows the reduction process of  $\text{Cu}(\text{III})$  to  $\text{Cu}(\text{II})$  while the C2 peak shown the reduction of  $\text{Cu}(\text{II})$  to  $\text{Cu}(\text{I})$  or  $\text{Cu}(0)$ . Fig. 3A and 3B show the cyclic voltammograms of Cu metal foil with one cycle and four cycles (continues cycle), respectively, where the same anodic peaks were recorded for both process. The only significant difference between the cyclic voltammograms of Fig. 3A and 3B are degradation of current density. For four cycle higher current density was observed at first cycle, and then increase for second, third and fourth cycle. Because Cu electrode not stability in  $1.0\text{ M KOH}$ . Cu metal is easily oxidized to form oxide compounds in the alkaline medium, which would formed oxide coating on the surface of the electrode,  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ , and  $\text{Cu}(\text{OH})_2$ , besides the other species depending on the potential, pH of the solution, the mass-transport conditions, ageing and surface restructuring processes [12].

Fig. 3 C, E, G and I shows cyclic voltammograms using Ni, Co, Pt and Ir composite electrode in  $1.0\text{ M KOH}$  (Ni and Co electrode) and in  $0.25\text{ M ethanol} + 1.0\text{ M KOH}$  (Pt and Ir electrode). Fig. 3 D, F, H and J shows cyclic voltammograms the effect of continues cycling using Ni, Co, Pt and Ir composite electrode in  $1.0\text{ M KOH}$  (Ni and Co electrode) and in  $0.25\text{ M ethanol} + 1.0\text{ M KOH}$  (Pt and Ir electrode).

Fig. 3 A, C, E, G and I shows cyclic voltammograms using Ni, Co, Pt and Ir composite electrode in  $1.0\text{ M KOH}$  (Cu-PVC, Ni-PVC and Co-PVC composite electrodes) and in  $0.25\text{ M ethanol} + 1.0\text{ M KOH}$  (Pt-PVC and Ir-PVC composite electrodes). Fig. 3 B, D, F, H and J shows cyclic voltammograms the effect of continues cycling using Cu-PVC, Ni-PVC, Co-PVC, Pt-PVC and Ir-PVC composite electrode in  $1.0\text{ M KOH}$  (Ni and Co composite electrode) and in  $0.25\text{ M ethanol} + 1.0\text{ M KOH}$  (Pt and Ir composite electrode). Fig. 3 D, F, H and J shows Ni-PVC, Co-PVC, Pt-PVC and Ir-PVC composite electrodes good stability for electrochemical oxidation in  $\text{KOH}$  solution.





**Fig. 3. Cyclic voltammograms (A, C, E, G, I) Cu, Ni, Co, Pt, Ir composite electrodes with one cycle, and (B, D, F, H, J) for Cu, Ni, Co, Pt, Ir composite electrodes with continues cycle at 5 cycle for Cu-PVC, 5 cycle for Co-PVC, Pt-PVC, Ir-PVC and 10 cycle for Ni-PVC, in 1.0 M KOH. Cyclic voltammograms Pt-PVC and Ir-PVC electrodes in 0.25 M ethanol + 1.0 M KOH. Scan rate of Cu-PVC: 10; Ni-PVC:30; Co-PVC: 10; Pt-PVC; 20 and Ir-PVC; 50 mV/sec**

Table 1 shows electrochemical activity and stability parameters for composite electrodes in 1.0 M KOH. The result from the cyclic voltammetry showed that the electrochemical activity and stability in alkaline solution using composite electrode is at a higher current density. This indicates that composite electrode gave a better electrochemical activity and stability for the electrochemical oxidation in KOH compared to solid electrode. The higher current density showed higher electrochemical activity [2]. From these cyclic voltammetry

experiments, the composite electrodes are suitable for electrosynthesis and fuel cell. Composite electrodes are more economical and beneficial for the oxidation of materials compared to solid metal electrode due to higher current density; hence more oxidation process will occur.

**Table 1. Data of activity and stability of composite electrodes**

Composite electrodes	Maximum current density (mA/cm <sup>2</sup> )	Activity	Stability
Cu-PVC	130.2	Large activity	No stability
Ni-PVC	12.5	Medium activity	Good stability
Co-PVC	45.3	Medium activity	Good stability
Pt-PVC	82.1	Large activity	Good stability
Ir-PVC	28.4	Medium activity	Good stability

**Chemical Stability of Electrodes**

The stability of electrode was analyzed using Atomic Absorption Spectroscopy (AAS). Analyzed have been done at three shares are solution, sponge formed on the electrode surface of anode and cathode. Table 2 shows metal concentration in solution and electrode surface (anode and cathode) or sponge, result of electrolysis 0.25 M ethanol by solid electrode, electrolysis time 6 h at potential constant 1050 mV, analyzed using AAS.

Table 2 shows that Co, Ni and Cu electrodes the higher corrosion compared the Pt and Ir metal electrode in alkaline solution. Ni metal electrode experience of the biggest corrosion at 0.1 and 1.0 M KOH. Co electrode at concentration 0.1 M KOH on the electrode surface formed sponge the higher concentration compared Ni and Cu electrode. Electrochemical oxidation of ethanol in 0.1 M KOH formed sponge on electrode surface with quantity of Co, Ni and Cu are 79.7 mg, 71.25 and 19.150 mg, respectively. If weight from the beginning Co electrode is 856.7 mg, hence a period of electrolysis 6 h, Co electrode formed sponge reach 9.32%. Sponge of a lot of formed on the electrode surface, if electrolysis ethanol in 0.1 M KOH. Electrolysis ethanol in 1.0 M KOH on electrode surface happened of the degradation sum up the sponge. Electrolysis ethanol in 1.0 M KOH using Cu electrode not formed sponge in anode surface, while in cathode a lot of formed of sponge.

Table 2 shows result of analysis chemical stability of composite electrode after used for the electrolysis of 0.25 M ethanol in 1.0 and 0.1 M KOH with electrolysis time 6 h at 1050 mV. In generally, metal content in solution very low for all composite electrodes. Although however, the forming of sponge on the electrode surface Co-PVC, Ni-PVC and Cu-PVC cause the corrosion also go into effect at composite electrode. Sponge a lot of formed at electrolysis ethanol in 0.1 M KOH especially at electrode surface of Co-PVC, Ni-PVC and Cu-PVC. Composite electrodes have the good stability in alkali solution. He is shown by lowering dissolve metal concentration during electrolysis.

**Table 2. Metal concentration in solution and electrode surface (anode and cathode) or sponge, result of electrolysis 0.25 M ethanol by composite electrode, electrolysis time 6 h at potential constant 1050 mV, analyzed to use AAS**

Type electrodes	KOH (M)	Metal concentration (mg) in		
		Solution	Electrode surface (anode)	Electrode surface cathode (Pt)
Co-PVC	0.1	0.982	49.700	0.486
	1.0	0.671	7.236	7.240
Cu-PVC	0.1	0.874	23.150	2.341
	1.0	0.562	-	17.591
Ni-PVC	0.1	3.775	65.452	-
	1.0	2.583	11.392	-
Pt-PVC	0.1	0.008	-	-
	1.0	0.023	-	-
Ir-PVC	0.1	0.000	-	-
	1.0	0.000	-	-

**Note: (-) not formed sponge**

#### IV. Conclusions

Ni, Co, Ir and Pt composite electrode higher stability compared to Cu composite electrode. Electrooxidation of ethanol in KOH solution using composite electrodes has shown good stability based on analysis using AAS. The composite electrode has shown higher current density in KOH solution.

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