

EFFECT OF ELECTRODE COMPOSITION ON THE MORPHOLOGY AND ELECTROCHEMICAL BEHAVIOR OF Ni-Cu-PVC COMPOSITE ELECTRODE

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Introduction

Electrocatalytic activity of copper and nickel materials strongly depends on their morphology, surface area, structure and composition, which would in turn depend on the preparation methods [1, 2]. The mechanical alloying technique to prepare cobalt–nickel alloys and to evaluate their performance for the ORR in alkaline media has been carried out [1, 3].

The filling of a polymer with metallic particles results in an increase in 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 [4]. One of the techniques of making porous electrode is by incorporating polymer material such as polyvinyl chloride (PVC) with the powder of respected metals [1]. Nickel and copper powders are widely used in numerous applications because they possess good catalytic, electronic and magnetic properties [5]. Ni powder, for example, has been used in catalysis for the direct cracking of methane, while CeO₂-supported copper catalysts have been tested for NO reduction. 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 are enhanced with respect to those of the pure metals.

Compared to nickel, copper shows lower overvoltage and higher enthalpy of OH⁻ absorption for the OER [6]. Thus, pure copper can be a good electrocatalyst for the OER. It indicates that the addition of copper to cobalt or nickel can increase the electrocatalytic activity for OER. The authors considered that the modification of electrode composition may change the morphology and electrochemical behavior (electrokinetics and electrocatalytic activity) of Ni-Cu-PVC composite electrode. Electrocatalytic activity for the oxidation of ethanol to acetic acid KOH solution will also be discussed.

Experimental

Preparation of nickel-copper-polyvinyl chloride (Ni-Cu-PVC) electrode

Five composite electrodes of Ni-Cu-PVC (95:0:5, 66.5:28.5:5, 47.5:47.5:5, 28.5:66.5:5 and 0:95:5) were prepared accordingly using mechanical alloying technique (MAT) with tetrahydrofuran (THF) used as the solvent [1]. The total weighed of the pellet obtained is approximately 1.5 g.

Apparatus and Procedures

Electrode surface was characterized using SEM and EDS on the JSM 5400 microscope equipped with a microprobe Voyager Noran system.

Universal Pula Dynamic EIS, Voltammetry, Voltalab potentiostat (Model PGZ 402) was used for electrochemical behavior measurement. Cyclic voltammetry experiments were performed in three electrodes system using Ni-Co-PVC, SCE and platinum wire, which acts as the working (anode), reference and counter electrode respectively.

The electrolysis process of ethanol was performed in 1.0 M KOH solution at room temperature in total 25 mL solution using 50 mL glass electrochemical cell.

Electrolysis products were analyzed using high performance liquid chromatography (HPLC) complete with two detectors set on line using C18 column. The acetonitrile in 0.1% H₃PO₄ were used as mobile phase throughout.

Results and Discussion

Cyclic voltammetry

Fig. 1 shows the cyclic voltammogram of Ni-Cu-PVC composite electrode in 1.0 M KOH solution at different percentages of Cu.

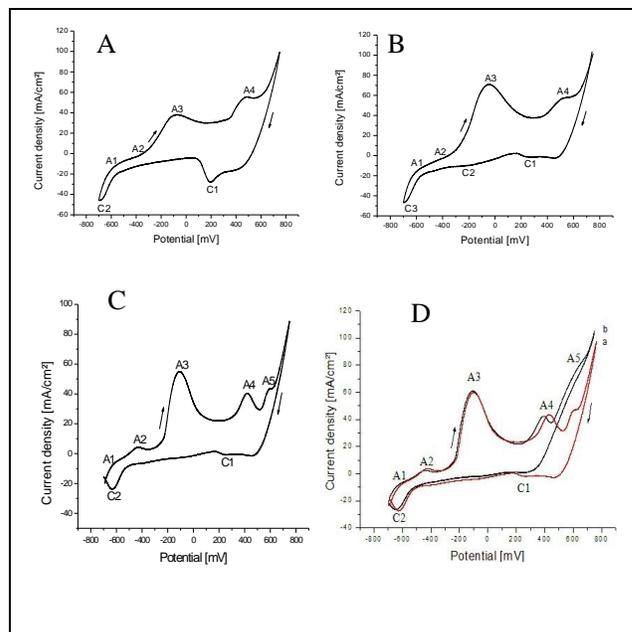


Fig. 1 Cyclic voltammograms of Ni_{95.0}Cu_{0.0}-PVC₅ (A) Ni_{66.5}Cu_{28.5}-PVC₅ (B) Ni_{28.5}Cu_{66.5}-PVC₅ (C) Ni_{47.5}Cu_{47.5}-PVC₅ and (D) C + 0.25 M ethanol 1.0 M KOH, scan rate 10 mV/sec

Figure 1A shows that A1, A2 and A3 peak represent the oxidation of Cu, while A4 peak is for the oxidation of Ni. A higher composition of Cu in the electrode leads to a higher A3 peak, while the A4 and C1 peaks are lower compared to the same peaks in Fig 1A (Fig. 1B). Figure 1(C) shows the CV voltammogram obtained when Ni_{47.5}Cu_{47.5}-PVC₅ electrode was used. Mixing of Ni and Cu with the same compositions caused both of the metals to have the same opportunity of being electrocatalysts, however, the overlapping of the A4 peak will occurred. Electrode prepared with the same composition of Ni and Cu caused the appearance of the A5 peak, which represents the oxidation of Cu (II) to Cu (III). However, in the presence of ethanol, there will be overlap with the ethanol oxidation peak (Fig. 1D). This showed that the oxidation of ethanol with Ni_{47.5}Cu_{47.5}-PVC₅ electrode can be done at a potential of 600 mV. A better electrocatalysts reaction would occur at the stated potential due to the formation of NiOOH and CuOOH on the surface.

The SEM micrograph of a freshly prepared Ni_{47.5}Cu_{47.5}-PVC₅ shows the rough, irregular and porous characteristic of the surface of the electrodes. This indicates that the surface morphology is highly heterogeneous and is composed of aggregates of nickel particles separated by gaps of PVC and voids between aggregate of nickel. These morphological, structure and porosity characteristics enable the usage of these composite electrodes as current collector for different catalysts with good adherence [7].

The kinetic parameters were determined using the Tafel plots. A linear region between 550-750 mV of the Tafel plots on the composition of the composite electrodes was identified. The Tafel slope was used to measure the rate of current changes and thus, the rate of the electrode reaction against the change in the electrode potentials. The Tafel slope obtained in the equal ration of this composite electrode (Ni_{47.5}Cu_{47.5}PVC₅) was approximately 690 mVdec⁻¹. The difference is due to the fact that the electrodes used in this work are porous and has a synergistic effect with high electrocatalytic activities [8]. By extrapolating the Tafel line, the exchange current density (i₀) could be obtained. The i₀ for Ni_{47.5}Cu_{47.5}-PVC₅ electrode was higher than the other electrodes composition as shown in Table 1.

Table 1 Kinetic parameters for the electrooxidation of 0.25 M of ethanol in 1.0 M KOH using different electrodes composition. Applied potential 1.05 V, electrolysis time 6 hour

Electrodes	b	i ₀ (mAcm ⁻²)	C	Energy consumption (kWh/ton)
Ni _{0.0} Cu _{95.0} -PVC ₅	581	2.129	83.13	4377.41
Ni _{95.0} Cu _{0.0} -PVC ₅	560	7.327	87.84	4681.00
Ni _{66.5} Cu _{28.5} -PVC ₅	380	7.568	93.96	4331.53
Ni _{28.5} Cu _{66.5} -PVC ₅	571	7.121	91.06	4811.17
Ni _{47.5} Cu _{47.5} -PVC ₅	690	8.154	98.72	4651.91

Note: b = Tafel slope (mVdec⁻¹), % C = Yield of acetic acid

The results obtained for the electrooxidation of ethanol in 1.0 M KOH at a constant potential of 1.05 V for 6 h shows a high percentage of acetic acid was produced with the Ni_{47.5}Cu_{47.5}-PVC₅ electrode compared to the other electrodes composition (Table 2). The results indicated that the catalytic activity and selectivity correlated with composition of the electrode.

Conclusions

The design of bimetallic electrodes, Ni-Cu-PVC electrode has results to a development of good electrodes in term of their electrokinetic's and electrocatalytic behavior. The electrocatalytic performance of Ni-Cu-PVC composite electrode used for the electro-oxidation of ethanol in alkaline solution was significantly improved due to their synergistic effect. The best performance is when the weight ratio of Ni to Cu is 1:1. Electron transfer process does not only occur outside the electrode during the electro-oxidation process, but also within the electrode itself depending on the metal used. The availability of PVC may contribute in the tranfer of electron from one metal to the other.

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