# Surface Modification of Glassy Carbon Electrode by Ni-Cu Nanoparticles as a Competitive Electrode for Ethanol Electro-Oxidation

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**ABSTRACT:** *In the present study, Nickel-Copper nanoparticles were electrodeposited on Glassy Carbon Electrode (GCE) by using electroplating deposition method. Prepared electrode was characterized by Scanning Electron Microscopy (SEM) and elemental mapping analysis. Results showed that Ni-Cu nanoparticles with a high density are distributed at the surface of a glassy carbon electrode. Subsequently, this electrode was applied for ethanol electro-oxidation using Cyclic Voltammetry (CV), ChronoAmperometry (CA) and Electrochemical Impedance Sectroscopy (EIS) techniques. The results of voltammograms showed high catalytic activity, increased the oxidation peak current density at the low potential for ethanol electro oxidation on Ni-Cu/GCE. Study of the electro-oxidation mechanism by the effect of scan rate for ethanol on Ni-Cu /GCE indicated that the oxidation process is controlled by diffusion processes. Chronoamperometric measurements illustrate that Ni-Cu/GCE exhibits a steady state activity for ethanol electro-oxidation. EIS measurements showed that the diameter of semi-circle for Ni-Cu/GCE is greatly smaller than the bare GCE. The modified electrode is a good candidate as an anode for application in direct ethanol alkaline fuel cells.*

**KEYWORDS:** *Electroplating; Nickel; Copper; Nanoparticle; Direct ethanol alkaline fuel cell*.

## INTRODUCTION

Renewable energy sources systems based on the Fuel Cell (FC) are an alternative energy system for stand-alone applications [1]. Among the fuel cells, the advantage of the Direct Alcohol Fuel Cells (DAFCs) operated at low temperatures between other FCs. DAFCs are important and able power source for portable electronic devices and fuel cell vehicles [1-4]. The liquid fuels is used in DAFCs includes methanol, ethanol as conventional sources of energy. Ethanol is less toxic compared to methanol, and more usable hydrogen as compared with methanol for application in the DAFCs [2-4]. This fuel (renewable energy source) is very easily produced by many biomass sources and agricultural wastes. Ethanol is extensively available and easy to storage. [5-8]. The investigation of Direct Ethanol Fuel Cells (DEFCs) have attracted many researchers and they have carried out to evaluate anode catalysts for DEFCs [7-10]. Ethanol Oxidation Reactions (EORs) presents encountered problems for the development of DEFCs. Higher performance electro catalysts lead to overcome this problem [9-11]. The electro catalyst is a great influence in improving the anode electrode for ethanol

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electro oxidation and lowering the cost. The type of electrocatalyst materials has been an important role as an anode in fuel cell efficiency [7, 8, 12]. Platinum (Pt) has been a major and mandatory component for most anode catalysts [12-14]. However, Pt is a costly noble metal and quickly self-poisoned by adsorbed intermediates [15, 16]. Therefore, Pt cannot be used in the future, hence, researchers have decided to use the alternative materials especially for next-generation fuel cells like DEFC. Nickel (Ni) is cheaper than Pt and has high electrocatalytic activity for oxidation of many fuels (ethanol and methanol) in alkaline medium [5, 17, 18]. Hence, we explore that Ni-Cu catalyzed in EORs is a promising field to apply for application in DEFCs. Previous researches results show that the performance of the ethanol electro oxidation could be significantly improved in alkaline media by Ni as electrocatalyst [17, 18]. Mechanism of ethanol electro oxidation in alkaline solution at Ni nanoparticles is as follow [17, 18]:

$$Ni + 2OH^- \rightarrow Ni(OH)_2 + 2e^- \quad (1)$$

$$Ni(OH)_2 \rightarrow NiOOH + H^+ + e^- \quad (2)$$

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \quad (3)$$

$$RH_2OH + NiOOH \rightarrow NiOOH(RCH_2OH)_{ads} \quad (4)$$

$$NiOOH(RCH_2OH)_{ads} + NiOOH \rightarrow Ni(OH)_2 + NiOOH(RCOH)_{ad} \quad (5)$$

$$NiOOH(RCHOH)_{ads} + NiOOH + OH^- \rightarrow 2Ni(OH)_2 + RCOO^- \quad (6)$$

*Tian et al.* [19] used nickel-copper as a catalyst for the electro oxidation of ethanol. The Ni–Cu alloy nanowire electrode exhibit excellent activity and stability toward EOR for application in DEFCs. *Shen et al.* [8] studied the synthesis of PdNi catalysts for the oxidation of ethanol in alkaline direct ethanol fuel cells. $Pd_2Ni_3$/C catalyst has been successfully synthesized by the simultaneous reduction method using $NaBH_4$ as reductant. Their cyclic voltammetry and chronopotentiometry studies showed that the $Pd_2Ni_3$/C catalyst exhibits a high catalytic activity for the electro oxidation of ethanol in an alkaline medium [8]. Recently, electro deposition is a suitable and controllable alternative method to synthesize metal nanoparticles such as Pt, Au, Pd, Ni and etc. Onto graphen support and at most electrode surfaces for the applicability as electro catalysis in DAFCs [5, 7, 20].

The surface of the glassy carbon electrode has a suitable substrate and extraordinary properties for electro deposited of metal nanoparticles [20-22]. The purpose of the present study is the catalytic activity evaluation of Ni-Cu nanoparticles (synergistic effect) at the surface of a glassy carbon electrode for ethanol oxidation. The catalytic activity of Ni-Cu/GCE was studied by electrochemical methods such as cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy.

## EXPERIMENTAL SECTION

### *Chemicals and reagents*

$NiSO_4$ (Merck), $CuSO_4$(Merck), ethanol (Merck, 96% purity), KOH (Merck, 84% purity), HF(Merck, 37% purity) and $HNO_3$(Merck, 69% purity) were used as received. All other chemicals were of analytical grade and used without further purification. Distilled water was used throughout.

### *Preparation of Ni-Cu/glassy carbon electrode*

The Ni–Cu nanoparticles were deposited on the glassy carbon electrode by electroplating with a galvanic deposition method. In first, the glassy carbon surface electrode was mechanically polished and then chemically etched by immersing in a mixture of volumetric 1:3:5 of HF: $HNO_3$:$H_2O$. The Ni–Cu nanoparticles were electrochemically deposited at the GCE surface from $NiSO_4$ (10 mM), $CuSO_4$ (10mM) and $KNa(C_4H_4O_6)$ (85 g/L). The deposition conditions were a current density of 5 mA $cm^{-2}$ for 6 min under pH 3.0 and the temperature is maintained at 27 $^oC$.

### *Physical characterization*

Morphology of the surface coating of the electrode was characterized by a Scanning Electron Microscope (SEM) (Model VEGAII, TESCAN) was employed with an accelerating voltage of 15 kV.

### *Electrochemical experiments*

Electrochemical techniques (CV, CA, EIS) were evaluated with an EG&G PARSTAT 2273 advanced electrochemical

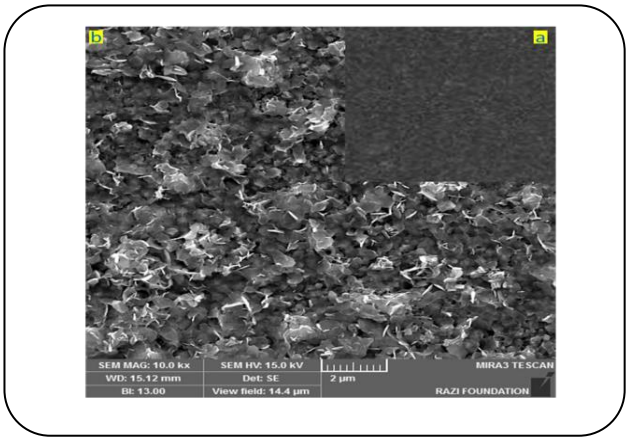


***Fig. 1: SEM images of bare GCE (a) and Ni-Cu/GCE (b) with the same magnification.***

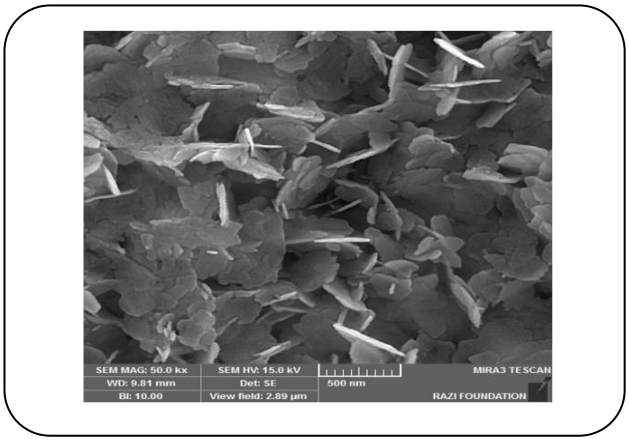


***Fig. 2: SEM image of Ni-Cu/GCE.***

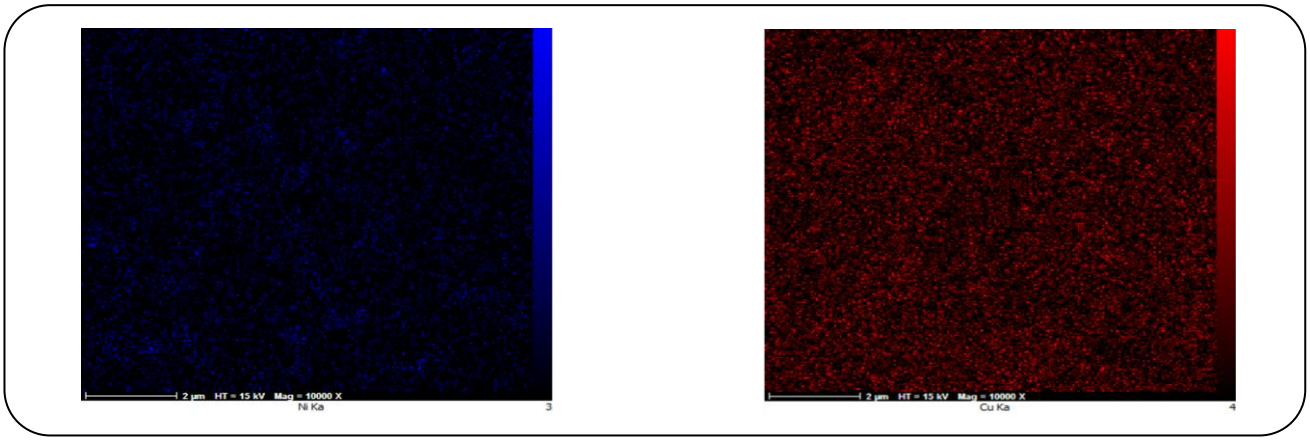


***Fig. 3: Elemental mapping Image of the Ni and Cu on GCE.***

systems. The electrochemical experiments were performed in a three electrode cell arrangement. A platinum sheet was used as the counter (auxiliary) electrode, while all potentials were measured with respect to the Ag/AgCl electrode. EIS measurements were done at the Open Circuit Voltage (OCV). The Root Mean Square (RMS) amplitude of modulation potential for the EIS measurements was 10 mV, and the frequency range was from 10 kHz to 50 mHz.

## RESULTS AND DISCUSSION

### *Characterisation surface of electrodes' morphology*

Fig. 1 illustrates the SEM micrographs of bare GCE and electrodeposited Ni-Cu nanoparticles at the surface of GCE. It can be seen that the Ni-Cu nanoparticles with a high density are distributed at the surface of GCE. Fig. 2 displays the morphology of the Ni-Cu nano particles at the surface of GCE. One can clearly see that the product consists of uniform well defined platelet-like particles with average lateral dimension size of 50-70 nm and a thin thickness. Fig. 3 shows the elemental mapping of Ni and Cu nanoparticles electrodeposited on bare GCE, in order to investigated their localaized elemental information which shows elements of Ni and Cu were well imobilized and almost uniformly distributed on the surface of glacy carbon electrod.

### *Electro-oxidation of ethanol on Ni-Cu/GCE*

The cyclic voltammetry method was used to identify the electro-catalytic behavior of the electrode. Fig.4(A) shows the cyclic voltammograms for Ni-Cu/GCE in 0.2 M KOH (a) and presence of 1M ethanol (b) at a scan rate of 20 m/Vs. It is observed from Fig. 4 (b) that the presence of ethanol anodic peak occurring at a low potential and increased the oxidation peak current density.

***Table 1: Comparison of the proposed method with reported methods for the ethanol electro oxidation.***

| Electrode | Preparation method | Region of potential (V) | Ref. |
|---|---|---|---|
| Ni hollow spheres (HS) electrode | Chemical reduction | -0.40 - 0 | [18] |
| GCE modified with [Ni:Al–Cl] | Chemical modified | +0.60 - +0.80 | [23] |
| Ni/MWCNT/Ch/WGE | Electro deposition method | +0.8 - +1.20 | [24] |
| Ni/NA/MWCNT/Ch/WGE | | +0.6 - +1 | |
| Ni–Cu nanowire electrode | Electro chemical reduction | -0.3 - +0.3 | [19] |
| Ni-Cu-NPs/glassy carbon | Electro deposition method | 0 - + 0.2 | our work |

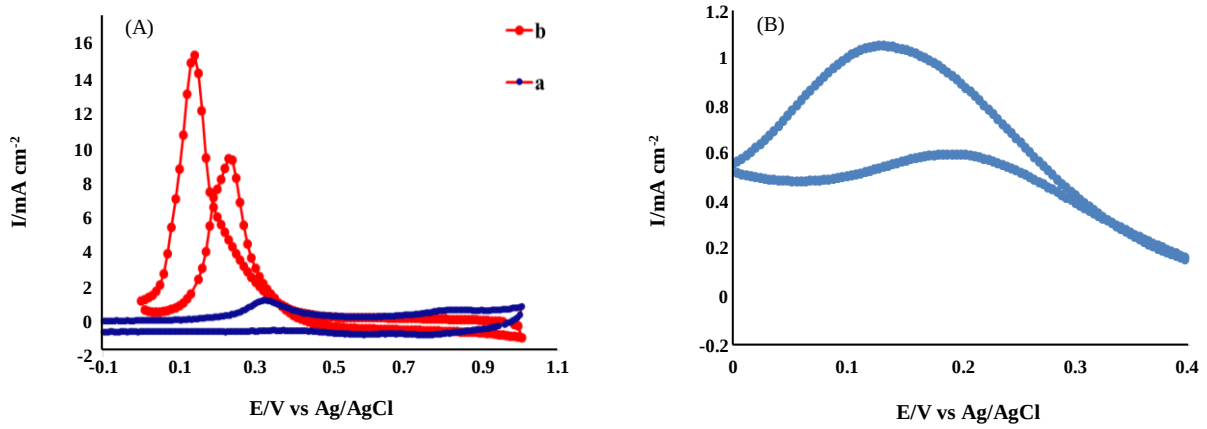


***Fig. 4: (A) Cyclic voltammograms of Ni-Cu/GCE in 0.2 M KOH in the absence (a) and presence 1M ethanol (b) at 27 ˚C in a saturated $N_2$ atmosphere: scan rate: 20 mV/s. (B) Cyclic voltammograms of Ni/GCE in.2 M KOH and the presence of 1M ethanol at a scan rate of 20 $mVS^{-1}$.***

Fig. 4(B) shows the cyclic voltammogram for Ni/GCE in 0.2 M KOH and presence of 1M ethanol at a scan rate of 20 mV/s. The current density of ethanol electro-oxidation on the Ni/GCE is less than that of the Ni-Cu/GCE.

### *Comparison of the proposed method with reported methods for the ethanol electro oxidation*

The comparison between the electrochemical characteristic of the Ni-Cu/GCE and some previously reported methods for the ethanol electro oxidation in Table 1. It was found that the proposed method showed advantag of low oxidation potential than to most methods.

### *Effect of scan rate*

Fig. 5 shows the cyclic voltammograms of the ethanol electro oxidation on Ni-Cu /GCE at different scan rates (20–100 mV/s) in the presence of 0.2 M KOH + 1M ethanol, the results of this test show that with increasing scan rate the potentials of the anodic peak shift to more positive potential value and with increasing in the electro-catalytic oxidation peak current density. For investigating the electro-catalytic reaction mechanism of ethanol oxidation on Ni-Cu /GCE that the diagram of peak current $i_p$ versus square root of sweep rate $\nu^{1/2}$ was plotted. As known in the precondition semi-infinite linear diffusion, peak current $i_p$ was related to scanning rate through the following equation [1, 25]:

$$i_p = (2.99 \times 10^5)\, n\, (\alpha n_a)^{1/2}\, A\, C_0\, D_0^{1/2}\, \nu^{1/2}.$$

Where $i_p$ is the peak current, $v$ is the scan rate, $n$ is the number of electrons transferred, $\alpha$ is the coefficient of electron transfer, $C_o$ is the bulk concentration of substrate, $D_o$ is the diffusion coefficient, $A$ is the electrode surface area. If the concentration $C_o$ holds constant, the peak current $i_p$ is linearly proportional to the square root of sweep rate $\nu^{1/2}$. It is seen from Fig. 6 that the peak current $i_p$ is linearly

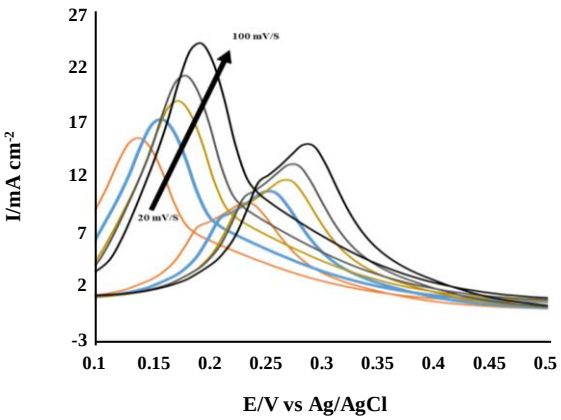


***Fig. 5: The cyclic voltammograms of ethanol on Ni-Cu/ GCE in 0.2 M KOH + 1M ethanol at different scan rate.***

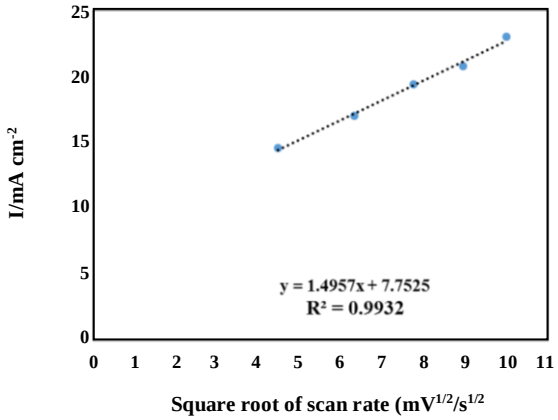


***Fig. 6: The plot of ethanol -electro oxidation peak current on the Ni-Cu/ GCE versus square root of scan rate $v^{1/2}$.***

This result indicates the ethanol electro oxidation reaction on the Ni-Cu/GCE electrode is controlled by the diffusion process [1, 25- 27].

***Electrode stability***

The electrochemical and physical stabilities of the Ni-Cu/GCE towards ethanol electro oxidation was studied by chronoamperometric measurement. Fig.7(A) shows the chronoamperometric curves of 0.2 M KOH +1 M ethanol solution on the GCE and Ni-Cu/GCE. It was found that the current for Ni-Cu/GCE is reduced to 0.27 mA after 330 seconds, the current tended to a constant value, which means the electrochemical performance of the prepared electrode is stable during the test time. Therefore Ni-Cu/GCE exhibits a steady state activity for ethanol electro oxidation in alkaline solution. Fig. 7(B) show cyclic voltammogram (a) and chronoamperometry (b) of the ethanol electro oxidation on Ni-Cu/GCE in 1 M ethanol solution. As explained in the text, the electro-oxidation of ethanol is performed better and more suitable in alkaline solution on the Ni-Cu/GCE. So, in 1 M ethanol solution, we see a lower current density and weaker stability.

***Electrochemical Impedance Spectroscopy (EIS) measurements***

The impedance spectroscopy is an applicable method for finding the properties of a surface modified electrode [1, 16, 22, 28]. Fig. 8 illustrates the results of impedance spectroscopy on the Ni-Cu/GCE and bare GCE in a solution containing 0.2 M KOH +1 M ethanol at the Open Circuit Voltage (OCV). As seen, the diameter of semi-circle for Ni-Cu/GCE is greatly smaller than the bare GCE. Presence of Ni,Cu nano particles leads to an increase in the rate of ethanol electro oxidation reaction.

**CONCLUSIONS**

Ni-Cu/glassy carbon electrode was successfully fabricated by using electroplating deposition method and characterized with scanning electron microscopy and elemental mapping analysis. The results indicated that Ni-Cu nanoparticles were homogeneously deposited on the surface of a glassy carbon electrode. The catalytic effect of the electrode for ethanol electro-oxidation was studied using electrochemical methods such as cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy. The cyclic voltammetry analysis of prepared Ni-Cu/GCE shows that anodic peak occurring at a low potential and increased the oxidation peak current density. The results of cyclic voltammograms at different scan rates for Ni-Cu /GCE indicated that ethanol electro oxidation reaction is controlled by the diffusion process. Chronoamperometric measurements illustrate that Ni-Cu/GCE exhibits a steady state activity for ethanol electro-oxidation. The low diameter of the capacitive arc was obtained that these particular advantage of the Ni-Cu/GCE are due to the simultaneous presence of Ni and Cu in the electrode composition. This electrode can be used repeatedly and exhibits stable electrocatalytic activity for ethanol electro oxidation. The modified electrode is an effective anode for application in direct ethanol alkaline fuel cells.

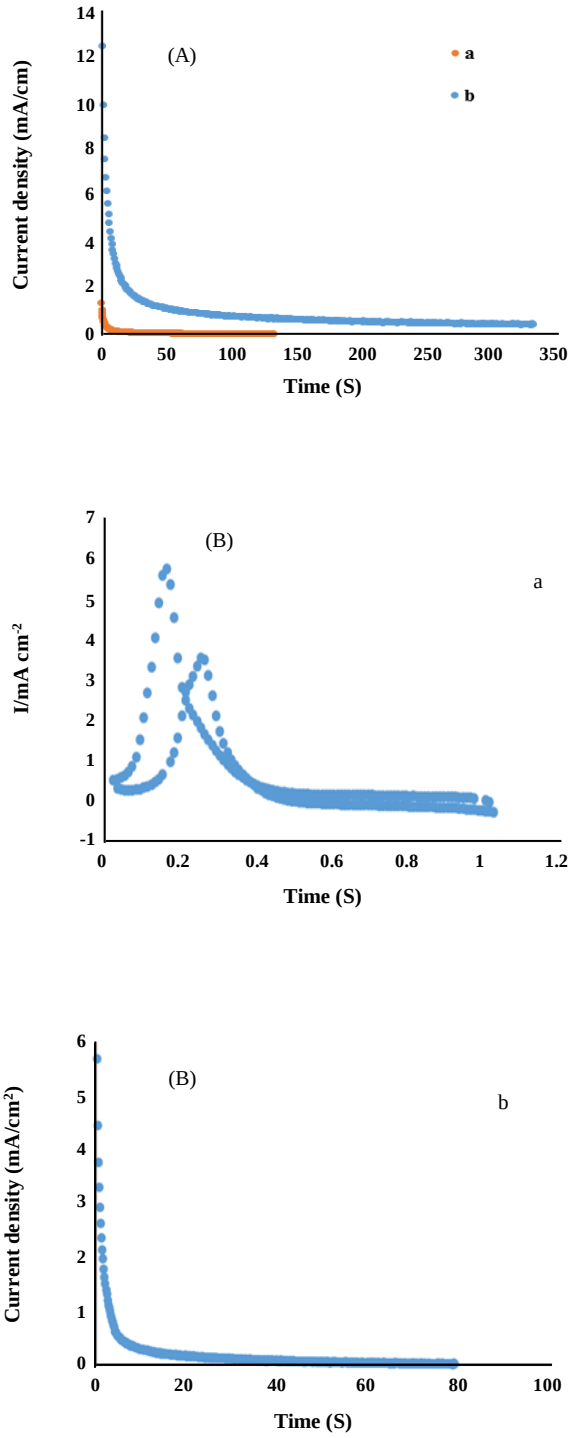


***Fig. 7: (A) Current–time curve for ethanol electro oxidation on GCE (a) and Ni-Cu/GCE (b) in 0.2 M KOH+ 1M ethanol. (B) Cyclic voltammogram (a) and chronoamperometry (b) of the ethanol electro oxidation on Ni-Cu/GCE in 1 M ethanol solution.***

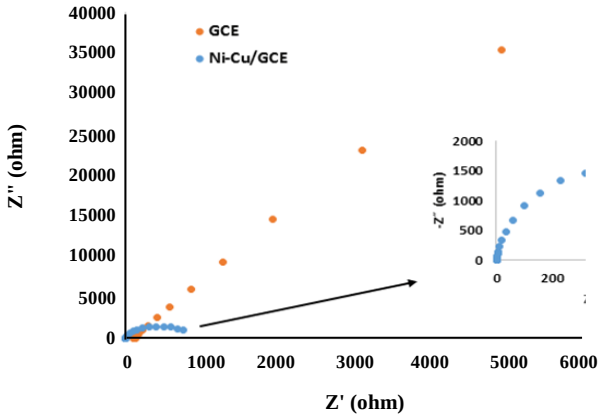


***Fig. 8: Impedance responses presented in Nyquist form for the GCE and Ni-Cu/GCE, at OCV, in 0.2 M KOH + 1M ethanol at 27°C in a saturated $N_2$ atmosphere.***

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**REFERENCES**

[1] Eshghi A., Kheirmand M., Graphene/NieFe Layered Double Hydroxide Nano Composites as Advanced Electrode Materials for Glucose Electro Oxidation, *Int J Hydrogen Energy*., **42**(22): 15064-15072 (2017).

[2] Liu Q., Liu M., Xu Q., Preparation and Electrocatalytic Characteristics of PdW/C Catalyst for Ethanol Oxidation, *Catalysts.*, 5(3): 1068– 1078 (2015).

[3] Eshghi A., Kheirmand M., Electroplating of Pt–Ni–Cu Nanoparticles on Glassy Carbon Electrode for Glucose Electro-oxidation Process, *Surface Engineering.*, **35**(2): 128-134 (2019).

[4] Tsivadze A.Y., Tarasevich M.R., Andreev V. N., and Bogdanovskaya V.A., Prospects of Low-Temperature Platinum-Free Fuel Cells, *Russian Journal of General Chemistry*., **77**(4): 783–789 (2007).

[5] Abdulah Mirzaie R., Eshghi A., Study of Methanol Electro-Oxidation on Ni and Ni–Pt/Carbon Paper Electrodes for Direct Methanol Fuel Cell Applications, *Surface Engineering.*, **30**(4): 263-267 (2014).

[6] Eshghi A., Kheirmand M., Sabzehmeidani M. M., Platinum–Iron Nanoparticles Supported on Reduced Graphene Oxide as an Improved Catalyst for Methanol Electro Oxidation, *Int. J. Hydrogen Energy*., **43** (12): 6107-6116 (2018).

[7] Wang Y., Zou S., Cai W.B., Recent Advances on Electro-Oxidation of Ethanol on Pt- and Pd-Based Catalysts: From Reaction Mechanisms to Catalytic Materials, *Catalysts*., **5**(3): 1507-1534 (2015).

[8] Shen S .Y., Zhao T.S., Xu J.B., Li Y.S., Synthesis of PdNi Catalysts for the Oxidation of Ethanol in Alkaline Direct Ethanol Fuel Cells, *Journal of Power Sources.*, **195**(3): 1001-1006 (2010).

[9] Yi Q.F., Chen Q.H., Yang Z., A novel Membrane-less Direct Alcohol Fuel Cell, *J Power Sources*., **298**: 171-176 (2015).

[10] Varcoe J.R., Slade R. C. T., Yee E. L.W., Poynton S. D., Driscoll J., Investigations into the ex Situ Methanol, Ethanol and Ethylene Glycol Permeabilities of Alkaline Polymer Electrolyte Membranes, *Journal of Power Sources.*, **173**(1):194-199 (2007).

[11] Serrà A., Gomez E., Montiel M., Valles E., Effective New Method for Synthesizing Pt and CoPt3 Mesoporous Nanorods. New Catalysts for Ethanol Electro-Oxidation in Alkaline Medium, *RSC Adv.*, **6**(53): 47931-47939 (2016).

[12] Wang Z.B., Yin G.P., Zhang J., Sun Y. C., Shi P. F., Investigation of Ethanol Electrooxidation on a Pt–Ru–Ni/C Catalyst for a Direct Ethanol Fuel Cell, *J. Power Sources.*, **160**(1): 37-43 (2006).

[13] Habibi B. Dadashpour E., Carbon-Ceramic Supported Bimetallic Pt–Ni Nanoparticles as an Electrocatalyst for Electrooxidation of Methanol and Ethanol in Acidic Media, *Int. J. Hydrogen Energy.*, **38** (13): 5425-5434 (2013).

[14] Razmi H., Habibi E. and Heidari H., Electrocatalytic Oxidation of Methanol and Ethanol at Carbon Ceramic Electrode Modified with Platinum Nanoparticles, *Electrochim. Acta.*, **53**(28): 8178-8185 (2008).

[15] Hosseini M., Sajjadi S., Momeni M.M., Electrodeposition of Platinum Metal on Titanium and Anodized Titanium from P Salt: Application to Electro-Oxidation of Glycerol, *Surface Engineering*, **23**(6): 419-424 (2007).

[16] Yao M., High-Performance Electrode Materials of Hierarchical Mesoporous Nickel Oxide Ultrathin Nanosheets Derived from Self-Assembled Scroll-Like a-Nickel Hydroxide, *Journal of Power Sources.*, **273**: 914-922 (2015).

[17] Kim J. W., and Park S.M, Electrochemical Oxidation of Ethanol at Nickel Hydroxide Electrodes in Alkaline Media Studied by Electrochemical Impedance Spectroscopy, *Journal of the Korean Electrochemical Society.*, 8: 117-124 (2005).

[18] Xu C., Hu Y., Rong J., Jiang S.P., Liu Y., Ni hollow Spheres as Catalysts for Methanol and Ethanol Electrooxidation. Electrochemistry Communications, *Electrochemistry Communications.* **9** (8): 2009-2012 (2007).

[19] Tian X., Zhao X., Zhang L., Yang C., Pi Z., Zhang S., Performance of Ethanol Electro-Oxidation on Ni–Cu Alloy Nanowires Through Composition Modulation, *Nanotechnology*, **19** (21): 1-6 (2008).

[20] Ye W., Zhang X., Chen Y., Du Y., Zhou F., Wang C., Pulsed Electrodeposition of Reduced Graphene Oxide on Glass Carbon Electrode as an Effective Support of Electrodeposited Pt Microspherical Particles: Nucleation Studies and the Application for Methanol Electro-Oxidation, *J. Electrochem.* Sci., **8**: 2122-2139 (2013).

[21] Brouzgoua A., Song S., Tsiakaras P., Carbon-Supported PdSn and $Pd_3Sn_2$ Anodes for Glucose Electrooxidation in Alkaline Media, *Appl. Catal. B: Environ*., **158** (1): 209-216 (2014).

[22] Danaee I., Jafarian M., Forouzandeh F., Gobal F. Mahjani M., Electro Catalytic Oxidation of Methanol on Ni and NiCu Alloy Modified Glassy Carbon Electrode, *Int. J. Hydrogen Energy*., **33** (16): 4367-4376 (2008).

[23] Ballarin B., Seeber R., Tonelli D., Vaccari A., Electrocatalytic Properties of nickel(II) Hydrotalcite-Type Anionic Clay:Application to Methanol and Ethanol Oxidation, *Journal of Electroanalytical Chemistry*., **463** (1):123-127 (1999).

[24] Jin G.P., Ding Y.F., Zheng P., Electrodeposition of Nickel Nanoparticles on Functional MWCNT Surfaces for Ethanol Oxidation, *Journal of Power Sources.*, **166** (1): 80– 86 (2007).

[25] Hosseini M., Momeni M.M., Gold Particles Supported on Self-Organized Nanotubular $TiO_2$ Matrix as Highly Active Catalysts for Electrochemical Oxidation of Glucose, *J Solid State Electrochem*., **14**(6): 1109– 1115 (2010).

[26] Hosseini M., Faraji M., Momeni M. M., Application of Titanium Oxide Nanotube Films Containing Gold Nanoparticles for the Electroanalytical Determination of Ascorbic Acid, *Thin Solid Films*., **519** (11): 3457– 3461 (2011).

[27] Eshghi A, kheirmand M., Palladium Nanoparticles Supported on Carbon Black Powder as an Effective Anodic Catalyst for Application in a Direct Glucose Alkaline Fuel Cell, *Iranian Journal of Hydrogen & Fuel Cell*., **1**: 11-17 (2016)

[28] Kheirmand M, Eshghi A., Electro Deposition of Platinum Nanoparticles on Reduced Graphene Oxide as an Efficient Catalyst for Oxygen Reduction Reaction, *Iranian Journal of Hydrogen & Fuel Cell*., **1**:1:7 (2015)