Development of Inexpensive High Energetic Electrodes Ni-Cu and Ni-CeO₂-Cu for Renewable Energy through Direct Ethanol Fuel Cell

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ABSTRACT

Application of fuel cell to produce renewable energy for commercial purpose is limited by the high cost of Pt based electrode materials. Development of inexpensive, high energetic electrode is the need of the hour to produce pollution free energy using bio-fuel through a fuel cell. Ni-Cu and Ni-CeO₂-Cu electrode materials, electro synthesized by pulse current have been developed. The surface morphology of the electrode materials is controlled by different deposition parameters in order to produce a high current from the electro-oxidation of the fuel, the ethanol. The developed materials are electrochemically characterized by Cyclic Voltammetry (CV), Chronoamperometry (CA) and Potentiodynamic polarization tests. The results confirm that the high current is due to their enhanced catalytic properties viz. high exchange current density (i_0), low polarization resistance (R_p) and low impedance. It is worthwhile to mention here that the addition of CeO₂ to Ni-Cu has outperformed Pt as far as the high electro catalytic properties are concerned; the exchange current density is about eight times higher than the same on Pt surface. The morphology of the electrode surface examined by SEM and FESEM exhibits that the grains are narrow and sub spherical with 3D surface, containing vacancies in between the elongated grains. The fact has enhanced more surface area for electro oxidation of the fuel, giving rise to an increase in current. Presence of Ni, CeO₂, and Cu is confirmed by the XRD and EDXS. Fuel cell fabricated with Ni-CeO₂-Cu material electrode is expected to produce clean electrical energy at cheaper rates than conventional one, using bio fuel the derived from biomass.

Keywords : Inexpensive high energetic electrode, Ni-CeO₂-Cu electrode, Ethanol oxidation, Cyclic Voltammetry, X-ray Diffraction

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1. Introduction

Demand of energy in the developed and developing countries, forces the burning of more fossil fuel, leading to a huge amount of polluting gases which are a threat to the life of man and animals. So the important challenge of today's scientist and researcher is to find a technology to produce clean alternative green energy at a cheaper rate. Fuel cell,

operated with the renewable fuels, is an alternative way to produce a clean renewable energy. The Fuel cell is an energy producing unit where fuels are electrochemically oxidized directly to electrical energy with high efficiency of energy conversion and minimum polluting gases [1]. Direct alcohol fuel cells (DAFCs) are one of the most important research areas for its appliance to the sustainable power systems such as portable electronic devices, electronic vehicles etc. [2,3]. In DAFCs, the liquid fuel, i.e. alcohol, is electrochemically oxidized at the anode and converted to the electrochemical energy. Among the alcohols, both methanol and ethanol find applica-

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tions in a fuel cell. The use of methanol in the direct methanol fuel cell is restricted due to its volatile and toxic nature [4]. But ethanol has certain advantages over methanol or other alcohols. It is nontoxic and has low vapor pressure, compared to the other biofuels [5] and hence can be easily transported and stored. Additionally, ethanol can be produced in great quantities by fermentation of sugar-containing agricultural materials [6-12]. The complete electro oxidation of ethanol that produces CO₂ along with 12 electrons is illustrated by the following reaction [10],

Anode:

Cathode:

Overall Reaction:

So the reversible cell potential is 1.144 V. So it is not any electrode potential vs. any RE. It is straight the Cell potentially determined by thermodynamic parameters. However due to kinetic factors, the net potential will be less than the thermodynamic reversible potential by various over voltages and IR drop as explained below:

$$E_{\text{net}} = E_{\text{rev}} - \eta_{\text{act}} - \eta_{\text{conc}} - IR_{\text{electrolyte}} \quad (4)$$

Where η_{act} is the total activation polarization due to anodic polarization, and η_{conc} is the total concentration polarization due to anodic and cathodic polarization.

The reaction mechanism of the ethanol oxidation depends on the electro-catalytic surface and the reaction medium [5,13,14]. Depending on the electrolyte medium, DEFCs can be categorized into two types: acidic DEFCs and alkaline DEFCs. Cremers et al. [14] reported that the electro oxidation of ethanol in alkaline medium is kinetically faster than that in acidic medium. The structure of the anode substrate plays a crucial function in the adsorption and electro oxidation of ethanol and other aliphatic alcohols [15]. In general Platinum (Pt) and Pt-based catalysts are

considered very good electro-catalyst material for low temperature alcoholic fuel cells [16]. However, using of Pt is limited, due to its cost and limited resources. Various works are being made to incorporate some non-Pt based metal oxides viz. NiO, CeO₂, Co₃O₄, Mn₃O₄ [3,17-19]. It is also suggested that an addition of Ni to Pd as Ni(OH)₂/NiOOH improves the apparent electro catalytic activity of the electrode in ethanol [20]. Nano-coated Ni-based alloys have also been investigated by Paul et al. [21,22] for inexpensive fuel cell electrode for energy applications. It has been reported that the rare earth oxide CeO₂ with cation vacancy state between +3 and +4, is a source of oxygen on the electrode catalytic surface and therefore enhances the electrode reactions. Thus the addition of CeO₂ to the metal electrode has been reported to enhance the electro-oxidation of alcohols by several times [23-26].

Keeping in mind with the research outcome of the above works on beneficial effect of Ni and CeO₂, present work is based on the development on Ni-Cu and Ni-CeO₂-Cu electrodes which are non Pt based and inexpensive. The materials are synthesized by the pulse current electro deposition technique and electrochemically characterized for high energetic electro catalytic properties and the structure by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Field-Emission Scanning Electron Microscope (FE-SEM) and Energy Dispersive X-ray Spectroscopy (EDXS).

2. Experimental Section

2.1. Material Pre-treatment and Chemicals

Cu-foil with the surface area of (1 × 1) cm² was polished by emery papers, degreased by acetone. It was washed in distilled water and dried. Electro deposition of Ni-Cu and Ni-CeO₂-Cu were carried out using DY 2300 potentiostat by pulse current (PC). For nickel coating, the electrolyte solution was 0.5 M nickel chloride hexahydrate (NiCl₂·6H₂O), 0.25 M nickel sulphate hexahydrate (NiSO₄·6H₂O), 0.5 M boric acid (H₃BO₃). Pre-selection of different deposition potentials was performed through several Potentiodynamic tests varying the composition of the electrolyte. CeO₂ was electro-coated using 0.1 M ceric sulphate (Ce(SO₄)₂·2H₂SO₄) and 0.2 M potassium chloride (KCl) electrolyte solution. The compositions of the electrolyte are given in Table 1.

Table 1. Electrolyte concentration

Chemicals	Concentration
Nickel Chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	0.5M
Nickel Sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	0.25M
Boric Acid (H_3BO_3)	0.5M
Ceric Sulphate ($\text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{SO}_4$)	0.1M
Potassium Chloride (KCl)	0.2M

Table 2. Electrode deposition Parameters for Ni and CeO_2 coating on Cu foil

	Potential varied (V vs SCE)	Optimum potential (V vs SCE)	Optimum Temperature	pH
For Ni coating	-0.31 V, -0.37 V, -0.6 V	-0.37 V	40°C	4
For CeO_2 coating	0.2 V, 0.5 V, 0.9 V	0.5 V	25°C	4.5

Electrode deposition Parameters for Ni and Ni- CeO_2 coating on Cu foil is also given in Table 2. The electrochemical characterization of the developed electrodes was carried out using 1 M ethanol in 1 M KOH solution.

2.2. Electrochemical Characterization

The performance of the developed electro catalytic Ni-Cu and Ni- CeO_2 -Cu oxide coated samples was characterized in ethanol solution, pH 13.1, by Cyclic Voltammetry, Chronoamperometry, and Potentiodynamic Polarization tests.

Cyclic Voltammetry of the electroplated sample was performed in a computer controlled electrochemical system machine, DY 2300 potentiostat, with a three electrodes system. The potential was scanned from -1.3 V vs. SCE to 0.3 vs. SCE with scan rate 50 mV/second to find out I_{max} (current amplitude). Here, Graphite rod was taken as counter electrode and saturated calomel electrode as reference electrode and test samples as working electrode. The Chronoamperometry (I vs. t) was tested in the same machine with different software. An experiment was carried out at different fixed potentials

selected around the ethanol oxidation potential as shown in Eqn. 1. The current (I) was monitored as a function of time (t) to find out how long the current is delivered from the cell.

A potentiodynamic polarization test was conducted with three electrode system as stated above and the electro kinetic parameters polarization resistance (R_p) and exchange current density (I_0) were determined from polarization curve. The potential was scanned between -1 V and 0.5 V vs. SCE at a scan rate of 1 mV/second. This experiment is also done using three electrodes system where Graphite rod was taken as counter electrode and saturated calomel electrode as reference electrode and test samples as working electrode.

2.3 Physical Characterization

The crystalline structure and crystalline phase of the electrodes are characterized by XRD. The test was done using Rigaku Ultima III X-ray diffraction for recording the diffraction traces of the samples with monochromatic $\text{Cu K}\alpha$ radiation at room temperature, at a scan rate of 2°/min. The crystallographic planes of X-ray diffraction were obtained from the inbuilt software of the X-Ray machine.

The surface morphology and particle distribution of the electrodeposited composite coatings were performed by using SEM (JEOL -JSM 6360) and FESEM (Hitachi S-4800 model) with accelerating voltage range 5-30 KV. The presence of electrodeposited Ni and CeO_2 particles was evaluated by using EDXS fitted with Scanning Electron microscope (JEOL -JSM 6360).

3. Results and Discussion

The electrode materials, Ni-Cu and Ni- CeO_2 -Cu were synthesized by controlling potential, current, and electrolyte chemistry by pulse current coating. A series of experiments was conducted to arrive at an optimum condition as depicted in Table 1 and 2. It is seen (Fig. 1) that the deposition potential for finer deposit depends on the characteristic of the potentiodynamic diagram in that particular electrolyte solution. The potential at the end of the Tafel region (i.e. -0.37 V vs SCE for nickel, Fig. 1) is found to be an optimum potential producing finer structure. At potential higher or lower than this, the rate of nucleation becomes less than the rate of growth. So less fraction

Fig. 1. Potentiodynamic polarization test to select the potential for deposition of Ni on Cu foil.

Fig. 2. Cyclic Voltammetry of different Nickel (Ni) coated Cu foil at temperature 40°C in 1M ethanol +1M KOH solution.

of finer deposit is likely to form. This is a point, which is the end of charge transfer mechanism and the beginning of mass transfer mechanism of an electrodeposition. It has been shown in the subsequent sections that the current delivered by an electrode synthesized at this potential is the highest. The similar potential for CeO_2 deposition is found out to be 0.5 V vs SCE, Table No. 2. The electrochemical characterizations of the materials electro synthesized under above specified condition are discussed in the following sections.

3.1. Study of Cyclic Voltammetry (CV)

Fig. 2 depicts the Cyclic Voltammetry of electrodeposited nickel at different potential at a fixed tem-

Fig. 3. Cyclic Voltammetry of Ni- CeO_2 -Cu foil and Pt in 1M ethanol + 1M KOH solution.

perature in ethanol solution. It is seen that for all the curves, there is a current maximum which signifies the highest rate of ethanol oxidation, delivering the maximum output current from the anode compartment of the fuel cell. It is interesting to note that the nickel, electroplated at -0.37 V vs. SCE, which corresponds to a point at the end of the Tafel region (Fig. 1), gives rise to maximum current. Paul [27] discussed the characteristics of the electro deposition at different points on the cathodic polarization line. It was explained that the point corresponding to a condition where the rate of nucleation is the highest and the rate of growth is the minimum, giving rise to finer and nano deposits.

3.2. Addition of CeO_2

It is seen that an addition of CeO_2 to Ni further enhances the maximum current in the CV study (Fig. 3). CeO_2 as reported by literature behaves like oxygen storage to adjust the oxygen concentration at the catalyst surface [26]. Another interesting fact of ceria is that it is a fluorite structure in which the cation (i.e. Ce) is in the valence state which can switch between +3 to +4. It retards the grain coarsening during the electro deposition and hence favors the nano nucleation. The fact is supported by SEM morphology of the structure as discussed in the subsequent section. It is also to be noted that at an intermediate potential at 0.5 V vs. SCE, the CV curve exhibits the maximum current. The computed cyclic voltammetry results are given in Table 3.

Table 3. Computed Cyclic Voltammetry results

Electrode Substrate	E_s (Onset Potential) V vs. SCE	E_p (Peak Potential) V vs. SCE	I_p (peak Current Density) mA/cm ²	$I_{at\ 0.3\ V}$ mA/cm ²
Bare Cu Foil	-0.538	-0.133	3.43	0.538
Ni coating at -0.31 V vs. SCE at 40°C	-0.553	-0.18	3.73	1.31
Ni coating at -0.37 V vs. SCE at 40°C	-0.531	-0.162	12.4	2.31
Ni coating at -0.6 V vs. SCE at 40°C	-0.572	-0.173	1.64	1.71
CeO ₂ coating at 0.2 V after Ni coating at -0.37 V vs. SCE at 40°C	-0.502	0.108	48.7	5.14
CeO ₂ coating at 0.5 V after Ni coating at -0.37 V vs. SCE at 40°C	-0.515	0.089	57.8	1.71
CeO ₂ coating at 0.9 V after Ni coating at -0.37 V vs. SCE at 40°C	-0.485	-0.017	33.6	0.961
Pt uncoated	-0.508	-0.267	10.9	1.44

Fig. 4. Chronoamperometry curve of ethanol oxidation reaction on Ni-Cu electrode at different potentials. **Fig. 5.** Chronoamperometry curve of ethanol oxidation reaction on Ni-CeO₂-Cu electrode at different potentials.

3.3. Chronoamperometry (CA) study of the developed electrode material

Having obtained the high current peak in the CV study for Ni-Cu and Ni-CeO₂-Cu electrodes; it is worthwhile to investigate the Chronoamperometry study to find out the nature of steady state current. Fig. 4 shows the chronoamperometry study for ethanol solution on electro coated Ni-Cu substrate at different potentials. It is seen that the current decreases initially and reaches a steady state within about 100 second and remains at the steady state current for a long duration.

So it gives an idea that this particular electrode can be used for a fuel cell for steady state energy. It is also to be noted in the Fig. 5 that the potential at which the steady state current is maximum (upper curve), is same as the potential at which the maximum current is exhibited in the CV study, Fig. 2. However the steady state current for the Ni is not high; it is in the order of 92-70 mA per 100 cm² electrode surface areas.

Similar figure is shown for electro coated Ni-CeO₂-Cu in Fig. 5. It is also seen here, that with the change of potential, the curve moves up or down without much

change of its nature. The steady state current reaches within about 30 s. It is interesting to find that the potential (56 mV vs. SCE) at which the maximum steady state current is achieved, is similar to that under CV study for this system (Fig. 3). It is also to be noted that the magnitude of the steady state current is as high as 2.5 times, the current produced on Ni- Cu electrode. It is estimated that a battery of 10 pair of fuel cells, fabricated with Ni-CeO₂-Cu of 100 cm² surface area, can deliver a of current 2.5 A with a cell potential of around 1 V using ethanol as fuel. So this opens up a cheaper pollution free energy producing unit, using ethanol or biomass derived bio ethanol.

3.4. Potentiodynamic Polarization Study

Potentiodynamic polarization tests are carried out to compute the electro kinetic parameters of the developed electrodes. Electro kinetic parameters, i.e. exchange current density and polarization resistance are calculated using Tafel equation [27-29]. Fig. 6 depicts the polarization curves of Ni-CeO₂-Cu electrode for comparison the curve for Pt and Cu foil has also been superimposed. While the nature of the all the curves same, the curve for Ni-CeO₂-Cu is the most right hand side curve that implies, it is giving the higher current for all over the potentials. It is to be noted that each of the curves, there is a current hump just above the reversible potential (E_{cell} reversible in the oxidation region). This current hump implies oxidation of ethanol on the different substrate materials [22,30]. The higher current for Ni - CeO₂-Cu electrode indicates that it is the best performing electrode substrate. The polarization resistance (R_p) and exchange current density (i_0) computed from the

Fig. 6. Polarization study of bare Cu, Pt, Ni-Cu and Ni-CeO₂-Cu electrodes in 1M ethanol+1M KOH solution.

polarization data have been illustrated by bar chart in Fig. 7 and Fig. 8 respectively. It is clearly indicated here that the exchange current density is the highest for Ni-CeO₂-Cu electrode and is about 2-3 times that of Pt which is known as very good electro catalytic material.

3.5. Material Characterization

3.5.1. X-ray Diffraction and EDXS analysis

Fig. 9 and 10 describe the XRD spectra for Ni-Cu and Ni-CeO₂-Cu electrodes. Ni peaks appears at 44.51°, 51.83°, 76.36° corresponding to (111), (200), (220) planes respectively along with Cu peaks. For Cu, XRD peaks appears at 43.24°, 50.40°, 74.23° which are corresponding to (111), (200), (220) planes respectively. XRD patterns for Ni-CeO₂ film (Fig. 10) consists of five main reflections on the 2θ scale,

Fig. 7. Comparison of Polarization Resistance of bare Cu, Pt, Ni-Cu and Ni-CeO₂-Cu electrodes in 1M ethanol + 1M KOH solution.

Fig. 8. Comparison of Exchange Current density of bare Cu, Pt, Ni-Cu and Ni-CeO₂-Cu electrodes in 1M ethanol + 1M KOH solution.

Fig. 9. XRD of Cu-Ni electrode.

Fig. 10. XRD of Cu-Ni-CeO₂ electrode.

28.62°, 33.07°, 47.45°, 69.30°, 76.69° corresponding to (111), (200), (220), (400), (311) planes respectively. Here also two Ni peaks appear at 39.50° corresponding to (311) plane respectively along with Cu peaks at 74.27° (220 planes). There are also another peaks of NiO of low intense observed at 37.64° and 50.56° corresponding to (-202) and (111) planes. Presence of Cu, Ni and CeO₂ surface atoms is confirmed by the Energy Dispersive X-ray Spectroscopy (EDXS) images, Fig. 11 and 12. The EDXS depicts the surface constituents while XRD reveals the total constituent materials in the system. It shows in both XRD and EDXS that the deposited materials are the atoms of Cu, Ni and CeO₂ on the surface as well as beneath it. The cerium is in the form of CeO₂ and nickel as free Ni as well as NiO.

Fig. 11. EDXS of Ni-Cu electrode.

Fig. 12. EDXS of Ni-CeO₂-Cu electrode.

3.5.2. SEM and FESEM Analysis

Fig. 13a and 13b show the morphology of the electro-coated Ni surface on Cu under Scanning Electron Micrograph (SEM) and Field Emission Scanning Electron Microscope (FESEM) respectively. While the SEM image of Ni does not provide much information, the FESEM image morphology clearly indicates that the grains are narrow and sub spherical with 3D surface. This means the effective 3D surface area is much more than the geometrical surface area. This accounts for an increase in current observed in previous sections. Similar studies of SEM and FESEM for Ni-CeO₂ are shown in Figs. 14a and 14b respectively. The morphology exhibits spherical Ni coating with CeO₂ well distributed throughout the matrix (Fig. 14a). The morphology is more clearly revealed in FESEM (Fig. 14b) which indicates elongated 3D structure with a vacancy in between two elongated grains That is the structure consists of grains along with nano channels and nano pores (3D) which effectively enhances the surface area for electrode reaction by several times. This explains the enhanced current and low polarization resistance, obtained on Ni-CeO₂-Cu electrode surface as found in Fig. 3, 7 and 8.

So the materials, electro synthesised by pulse current coating method consists of the above constitu-

Fig. 13. (a) SEM image, (b) FESEM image of Cu-Ni.

Fig. 14. (a) SEM image, (b) FESEM image Ni-CeO₂-Cu.

ents. The grains are in the nano to micro range with channels in 3D that provides a huge surface area for a fixed geometry. The fact makes it a high energetic electrode surface with enhanced current on electro oxidation of ethanol.

4. Conclusion

From the foregoing result and discussion, it is seen that an energetic and high electro-catalytic fuel cell electrode material Ni-CeO₂ has come up. Its performance as a fuel cell electrode material in DEFC is much superior to that of the precious metal Pt. The material is cheaper material compared to Pt. This present investigation throws a new light for renewable energy synthesis through fuel cell from ethanol or bio ethanol derived from bio-mass at a cheap and economical viable price for commercialization.

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