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Electrochemical Characterization of Few Electro-Synthesized Fuel Cell Electrodes to producing Clean Electrical Energy from Alternative Fuel Resources

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Abstract:

The increasing cost of energy associated with a higher production of polluting necessitates alternative green energy resources. Fuel cell is one such electrochemical energy producing unit to produce clean electrical energy with very high energy conversion efficiency. It has not been commercialized due to the high cost of Pt based electrode material. Thus the major challenge in the development of fuel cell is to produce inexpensive and high energetic electro catalytic electrode materials. The present investigation deals with the development of a few electrode materials; Ni-Co-Fe, MnO_2-C, ZnO-Al_2O_3 and Ni-CeO_2-Cu which were developed by electro-synthesis at an optimum current density, potential and electrolyte chemistry, determined by a series of experimentation. The electrochemical oxidation of a few fuels: methanol, ethanol, and glucose, on these developed electrodes were characterized by Polarization, Cyclic Voltammetry, Chronoamperometry tests. It was found that all these electrodes performed very well with low polarization resistance, and delivered a high current in the order of 30-60 mA/cm^2 from the electro oxidation of the fuels. The electrode Ni-CeO_2 has outperformed all other materials including Pt. The materials were characterized by XRD which confirms the constituents of alloys and composite metal oxides. The SEM studies exhibit grain refinement of Ni-CeO_2 due to CeO_2 addition. The fact that the fine grains with recess in between the grains, producing more effective surface area in 3D, accounts for fast electrochemical oxidation of the fuel and generation of a high current.

Keywords: alternative energy, electro-catalytic materials, potentiodynamic polarization, cyclic voltammetry, SEM, XRD

1. Introduction:

The demand for energy is increasing everyday, leading to more use of coal and crude petroleum product to produce energy. But the energy synthesis through coal, oil and gas is associated with huge pollution problems and greenhouse effects. So the major challenges for scientist and researchers are to produce pollution free renewable energy from alternative fuel resources such as biomass, water, solar system which are renewable. Although there are abundance of biofuels production from different biomass, the fuel oil produced is chemically oxidized to heat to mechanical or electrical energy. The energy conversion by this method is of low efficient. In fuel cell where fuel is electrochemically oxidized directly to electrical energy, the energy conversion efficiency is very high . Direct Alcoholic fuel cells (DAFCs) [1-3] are one of the alternative clean energy technologies by the electro oxidation of the alcohols. Among the different possible alcohols, Yuan et al [4] reported that methanol is the most promising fuel because its use as a fuel has several advantages in aqueous electrolytes, available at low cost, easily handled, transported and stored. Other alcohols such as ethanol also have been considered for use in fuel cells as reported by many authors [5-8]. S.Q Song and P. Tsiakaras

[9] were informed that ethanol is less toxic compared to methanol, and can be easily produced in great quantity by fermentation of sugar-containing raw material. C. Lamy and J-M. Le´ger [10] determined the theoretical mass energy density of the fuel methanol and ethanol and the calculated mass energy densities are 6.1 kWhKg^{-1} and 8.1 kWhKg^{-1} respectably. For this consideration these are very good candidates for fuel in fuel cell. Glucose is another alternative sources of clean energy for today's scenario as it is cheap, easily obtainable, nontoxic and non-flammable. Complete oxidation of glucose would have produced much more energy (2.87 × 10^6 joule/mole energy than that its partial oxidation. Several authors [11, 12] reported that the fuel cell operates at low temperature and hence can be easily used in portable devices etc.

The main science and engineering for fuel cell development is to produce high electro catalytic energy materials, on which the fuels are electrochemically oxidized releasing electron at a fast rate that gives rise to current and energy from the cell. A number of researchers [13-22] reported that the precious group metals and alloys such as Pt,Pt/C, Pt-Ru, Pd, Pt-Ru-Pd, Pt–Sn/SnO_2, Au act as very good electrodes for fuel cell. F. Vigier et al [13] and S. Meenakshi et al [14] investigated electrooxidation of ethanol on Pt based electrode such as Pt-Sn, Pt-Re dispersed on carbon powder or carbon supported Pt-Sn/SnO_2. They reported that the performances of these catalysts are very encouraging for ethanol electro-oxidation in direct ethanol fuel cells. On the other work ethanol and methanol oxidation on Pd in alkaline solution was studied by Z.X. Liang et al [15] and Dongyao Wang et al [16]. The electrochemical oxidation of methanol on Pt or Pt based alloys such as Pt-Ir-IrO_2NT [17], Pt-Ru/C [18], np-PtPdAlCu [19], nPtRuMo/C [20] was studied in different medium. The performance of these electrodes material shows that these can be a good alternative to be used as electrode materials of low temperature methanol fuel cells. X. Yan et al [21], Mauro Pasta et al [22] studied on Pt and Gold electrodes for glucose oxidation in different electrolyte medium and its electrocatalytic activity was evaluated. But these precious metals are very expensive that hinders the developments of fuel cell to the next generation for producing energy at an economical rate in the domestic and industrial sectors. So quantity of the amount of precious materials needs to be reduced or non Pt based inexpensive material need to be developed. People have tried to developed electrode material with precious metal in combination of inexpensive base metals. Paul et al. [8] produced nano porous anodized aluminum (Al) where pore are filled up by precious metal through electrodeposition. Among the non Pt based electrode material, Ni-based alloys, MnO_2, and ZnO, CeO_2 show very good electrocatalytic properties and are used as electrode in battery and experimental fuel cell. Riyanto et al [23] and Andre´ia Cristina Furtado et al [24] have studied ethanol oxidation on Cu and Ni surface. They found that these two electrode materials act as a good anode material for electro-oxidation of ethanol. It has been reported that the rare earth oxide CeO_2 acts as a source of oxygen on the electrode catalytic surface and therefore enhances the electrode reactions [25]. Addition of CeO_2 to Pt or other precious metal electrodes has been reported to enhance the electro-oxidation of alcohols by several times [26, 27]. On the other work Lei Li et al [28] and Slaughter et al [29] reported that MnO_2 or ZnO coated gold electrode have very excellent elctrocatalytic properties for fuel oxidation.

The present paper deals with electrochemical characterization of Ni-Co alloys, MnO_2-C, ZnO-Al_2O_3, and Ni-CeO_2-Cu in the form of potentiodynamic polarization test, cyclic Voltammetry (CV), Chronoamperometry. The morphology of the electro synthesized materials was studied by electron microscope. The presence of the electro deposited materials is confirms by X-ray diffraction (XRD) analysis. The surface morphology is studied by scanning electro-microscope (SEM).

2. Experimental:

2.1. Materials Pre treatment:

Three different materials are chosen for electrode deposition namely, Al foil, 304SS, and Cu foil. The materials were polished by emery papers, degreased by acetone and then electro-polished in a solution of perchloric acid and ethanol. It was washed in distilled water and subsequently pre-treated by dipping in 12.6% NaOH for 2 min, rinsing in double distilled water finally dried.

2.2. Electro-deposition:

Electro deposition of different metals and metals oxide on the materials were carried out using HY3002 Potentiostat. The pretreated samples were electrodeposited from the different solutions of salts at an optimum composition of the metal salts, at fixed pH value, temperature, cell potential and galvanic current density. The optimum conditions were found out by a series of experiments, varying each of them over a range (Table 1).

2.3. Electrochemical Characterization:

The performance of the developed electro catalytic metal and metal oxide coated sample was performed in different solution such as Methanol, Ethanol, and glucose in phosphate buffer at pH 7.4 by Potentiodynamic polarization tests Cyclic Voltammetry (CV), Chonoamperomety (CA).

Table 1. Optimum parameters for electro synthesis of different electro coated materials

Chemicals Name (Concentration)	pH	Applied potential (V)	Applied current density (mA/cm^2)	Temp (°C)	Time (Sec)
For Ni-Co-Fe coating on Al-foil					
Nickel sulphate($NiSO_4 \cdot 7H_2O$) ($0.26 mol.L^{-1}$) Nickel chloride($NiCl_2 \cdot 6H_2O$) ($0.06 mol.L^{-1}$) Cobalt sulphate($CoSO_4 \cdot 7H_2O$) ($0.078 mol.L^{-1}$) Formaldehyde(HCHO) ($0.5 mol.L^{-1}$) Ammonium sulphate ($(NH_4)_2SO_4$) ($0.3 mol.L^{-1}$) Boric acid(H_3BO_3) ($0.4 mol.L^{-1}$)	3.2-3.7	5.5-6.5	50	30-35	600
For MnO_2-C coating of SS304					
Manganese sulphate ($MnSO_4$) (0.34M) Sulphuric Acid (H_2SO_4) (0.6M) Carbon powder (1.2gm/100ml)	11.6-13.6	4-6	165	60	360
$ZnO-Al_2O_3$ coating on Al foil					
Zinc Chloride ($ZnCl_2$) (0.5M) Potassium Chloride KCl (0.2M)	5	4.1-5.7	150	40	240
Ni-CeO_2 coating on Cu foil					
Nickel chloride $NiCl_2.6H_2O$ (0.5M) Nickel sulphate $NiSO_4.6H_2O$ (0.25M) Boric acid H_3BO_3 (30gm/liter) Ceric sulphate $Ce(SO_4)_2.2H_2SO_4$ (0.1M) Potassium Chloride KCl (0.2M)	4-4.5	Ni coating at -0.37V whereas CeO2 coating at 0.5V	-	Ni coating at 40°C whereas CeO2 coating at 25°C	300

2.4. *Polarization Test:*

Potentiodynamic Polarization experiment was conducted using a Gamry Potentiostat instrument coupled with Echem analyst software, controlled by a personal computer, in a conventional three electrodes cell systems cell. The working electrode was electro deposited metal and metal oxide coated electrodes, the graphite as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The later was connected to electrochemical cell through a lugging capillary whose tip was placed close to working electrode surface to minimize IR drop. Potentidynamic polarization experiment with electrodeposited electro catalyst surface, developed at an optimum electroplating condition (Table 1), were performed in different fuel solutions i.e. methanol, ethanol, glucose to determine the various electrochemical parameters viz. exchange current density I_o, polarization resistance (R_p), β_a, β_c etc. The potential was scanned between selected potential regions at a scan rate of 1.0 mV/s.

2.5. *Cyclic Voltammetry (CV):*

Cyclic Voltammetry of the electroplated sample was performed in a computer controlled electrochemical system machine, DY 2300 Potentiostat, with a three electrode system to find out I_{max} (current amplitude). Here, the graphite rod was taken as counter electrode and saturated calomel electrode as reference electrode and test sample as working electrode. The potential was scanned between selected potential regions of different electrodes at a scan rate of 50 mV/s.

2.6. Chronoamperometry (CA):

The Chronoamperometry (CA) was tested in the same machine with different software. Experiment was carried out at different fixed potentials selected around the range of different fuel oxidation potential. The current (I) was monitored as a function of time (t) to find out how long the steady state current is delivered from the cell.

2.7. Physical Characterization

2.7.1. X-Ray diffraction (XRD):

The X-ray diffraction technique is carried out to develop an idea about crystalline structure and crystalline phases in each coated surface. The test was done using a Rigaku Ultima III X-ray diffraction unit for recording the diffraction traces of the samples with monochromatic Cu K_α radiation at room temperature. The scan rate was of 2^o/min. The crystallographic planes of XRD were obtained from the inbuilt software of the X-Ray machine. The electroplated samples were rinsed with pure water and then washed with acetone and kept in desiccators at room temperature before this analysis.

2.7.2. SEM:

SEM Micrographs of the investigated samples were photographed using JEOL -JSM 6360 Scanning Electron microscope (SEM) at different magnification and high resolution.

3. Results and Discussion:

Energy conversion from fuel to pure electrical energy in a fuel cell is dependent on electro catalytic property of the electrodes, Anode and cathode, in the cell. The electrochemical oxidation of the fuel in the anodic chamber is carried out by the anode which drags the electron from the fuel and passes it to the external load and then to cathode. The rate of this process decides the magnitude of the current and hence energy generated by the cell. And this rate is dependent on how good is the anode that is the electrocatalytic property of the anode. While the cathode in the other chamber takes up the released electron from the anode and uses it to reduce the ionized fuel say , H^+ to H_2O , using the atmospheric oxygen. So the cathode must have the capacity to take up the electron and do this process fast so that the circuit is complete and the cell produces high current and cell potential with minimum loss due to electrode polarization. The present paper aims at finding which electrode performs the best for a given fuel.

3.1. Potentiodynamic Polarization Test:

The electrolytic properties of this anode and cathode are tested by different electrochemical experiments. One of the important tests is the potentiodynamic polarization which gives electrokinetic parameters of the given electrode with the fuel and hence the overvoltage factors which reduces the net current and cell potential.

Figure 1.(a-d) depicts polarization curves of the different electrodes, developed by electro synthesis process. Since Pt is considered as natural a high electro catalytic material but expensive, the performances of these electrodes are compared with that of Pt. It is seen that all the curves for the coated materials shift to the right in comparison to those for bare surface materials. The shifting of the curve to the right indicates more current (X-axis) generated from the lector oxidation of the fuel on that particular anode surface. So this shows the coated electrodes developed perform better than the uncoated ones. It is also to be noted that some of the materials produce higher current compared to Pt in methanol, glucose or ethanol solution. The electro kinetic parameters computed from the polarization data are depicted in Table-II. Two important parameters, exchange current density and polarization resistance are very much prominent. The higher the exchange current density and the lower is the polarization resistance, the superior is the electrode to produce a high current with minimum energy loss. It is interesting find the high exchange current density for the most electrocoated electrodes with lower polarization resistance. The data are plotted in a bar chart in fig.2.

It is clearly reflected in all the bar chart, that the exchange current density is the highest for electro deposited Ni-CeO_2, MnO_2-C, ZnO-Al_2O_3 materials in the ethanol and glucose solutions respectively (fig. 2b, 2c, 2d). However exchange current density of Ni-Co and Ni-Co-Fe electrode material in methanol solution is very comparable to the Pt. Three new electrodes are to be marked here; Ni-CeO_2 in ethanol, ZnO-Al_2O_3 , and MnO_2-C in glucose fuels. Synthetically produced bioethanol and glucose from waste vegetable [30,31]are available in abundant. These electrodes exhibit high energetic electrocatalytic property superior to that of Pt which is known as a very good electro catalytic material.

Having achieved high electro catalytic property for Ni-CeO_2, MnO_2-C, ZnO-Al_2O_3 electrodes, more emphasis is given for further tests like Cyclic Voltammetry and Chronoamperometry for these materials in the following section.

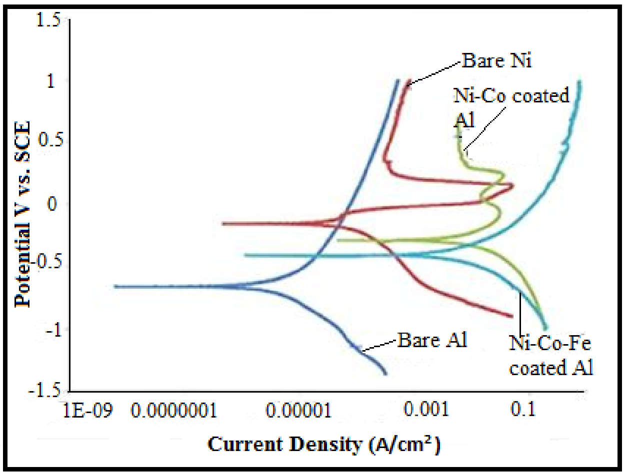

Fig.1.a. Polarization study of bare Al, bare Ni, Ni–Co, and Ni–Co–Fe coated Al in methanol solution

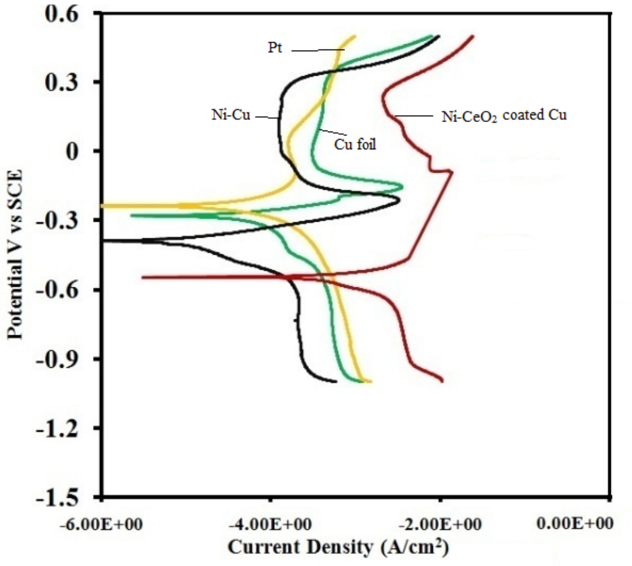

Fig.1.b. Polarization study of Pt, Ni and Ni-CeO_2 coated Cu foil and pure Cu foil electrodes in 1M ethanol + 1M KOH solution

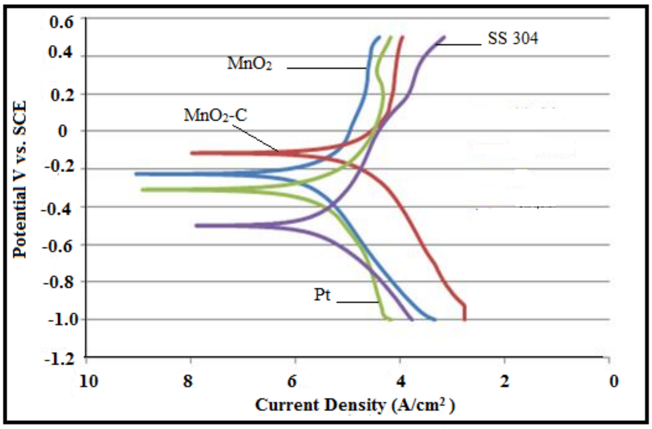

Fig.1.c. Polarization study of 304SS, Pt, MnO_2 and MnO_2-C coated stainless steel electrode in 0.5M glucose + 1M KOH solution.

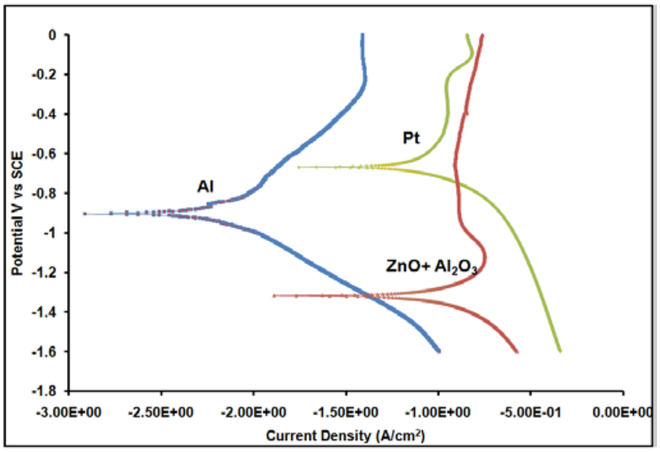

Fig.1.d. Polarization study of Pt, ZnO-Al_2O_3 coated and pure Al foil electrodes in 0.5M glucose solution in phosphate buffer solution

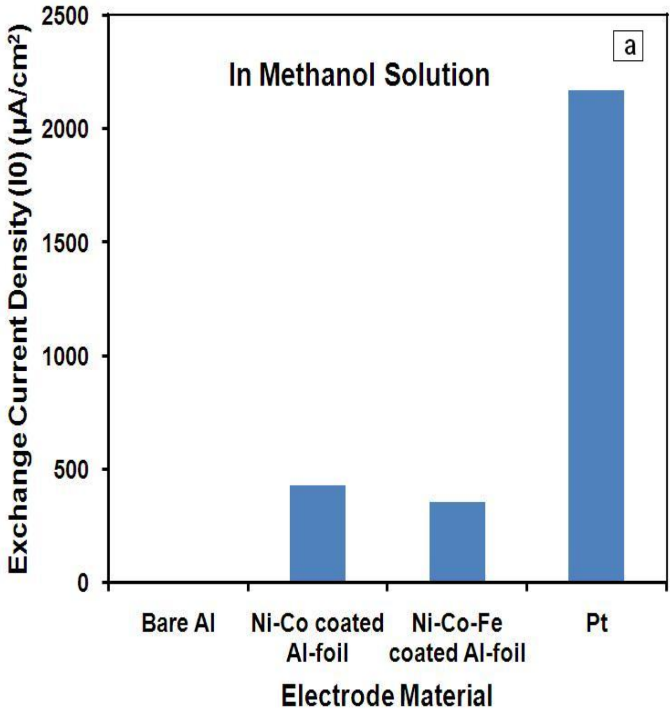

Fig. 2.a. Comparison of exchange current density of different electro synthesized electro coated materials in methanol solution

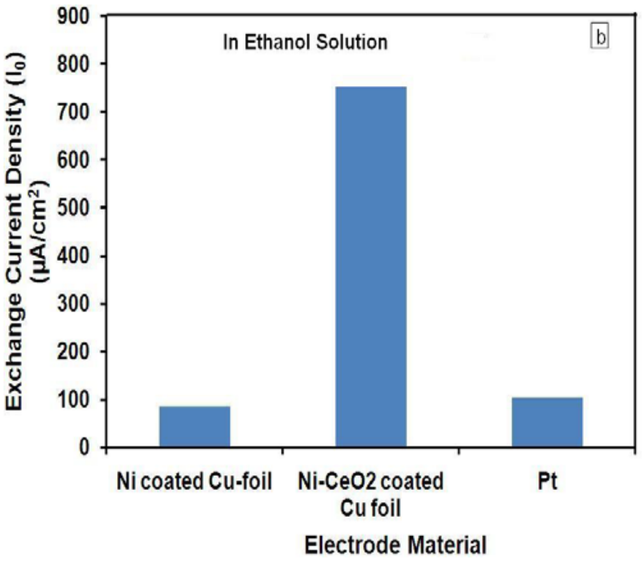

Fig. 2.b. Comparison of exchange current density of different electro synthesized electro coated materials in ethanol solution

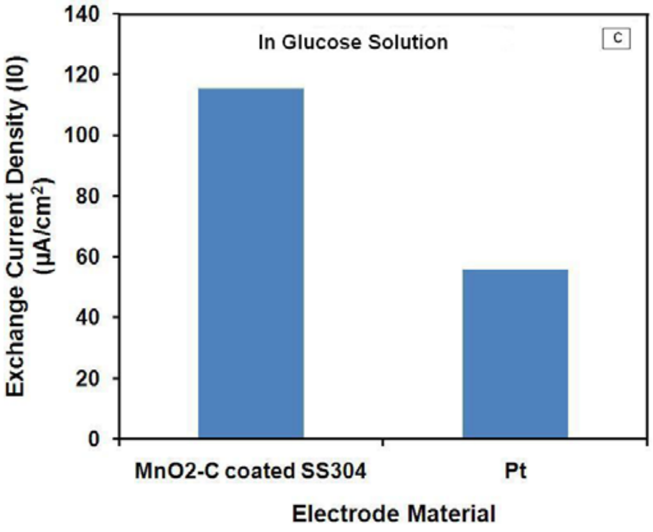

Fig. 2.c. Comparison of exchange current density of different electro synthesized electro coated materials in glucose KOH solution

3.2. Cyclic Voltammetry (CV):

The CV study exhibits the maximum current at the oxidation potential of the fuel for a particular electrode surface. Fig.3a, 3.b, 3.c depicts Cyclic Voltammetry studies of electro coated Ni and Ni-CeO$_2$ coated Cu foil ,MnO$_2$, MnO$_2$-C , ZnO-Al$_2$O$_3$ and Platinum in 1M ethanol solution and 0.5M glucose fuel cell solution respectively. It is seen that the oxidation takes place at the highest rate where there is a current jump. The current is the flow of electron, released from the oxidation of fuel. So higher the current, faster is the rate of oxidation on the particular substrate at the potential. The magnitude of this current jump I_{max} decides

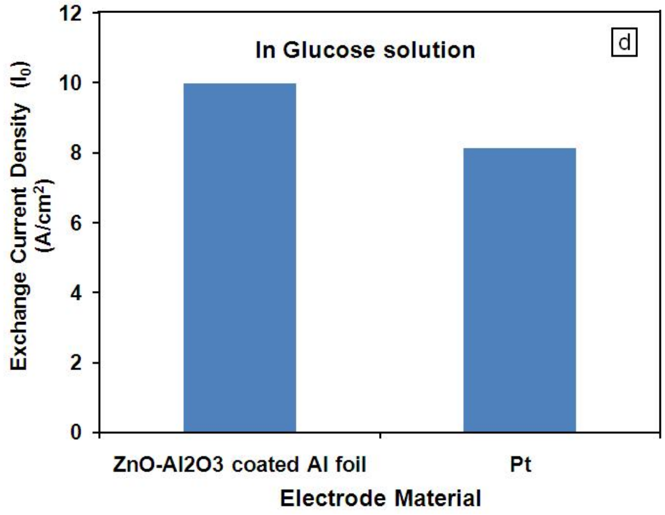

Fig. 2.d. Comparison of exchange current density of different electro synthesized electro coated materials in different glucose phosphate buffer solution.

Table 2. Computed electrochemical kinetic data for different electrode in different solution

Electrode Substrate	β_a (mV)	β_c (mV)	Exchange Current Density (I_0) (A/cm^2)	Polarization Resistance (R_p) (ohm)
In methanol solution				
Ni–Co–Fe	307	–369	0.355×10^{-3}	17.48
Pt	356.3	455	2.1×10^{-3}	26.63
In ethanol solution				
Ni-CeO_2-Cu	210.1	256	0.769×10^{-3}	33.4
Pt	230	170	0.1×10^{-3}	255
In glucose KOH solution				
MnO_2-C	131.7	112	0.115×10^{-3}	226
Pt	111.0	100.2	0.059×10^{-3}	469
In glucose phosphate buffer solution				
ZnO-Al_2O_3	160	100	9.98	2.4618×10^{-4}
Pt	250	190	8.139	3.0204×10^{-4}

the quality of electro catalytic property of electrode substrate. The rate of electrochemical oxidation will be highest on a substrate which exhibits maximum current. It is seen from the figures that the electrodes MnO_2-nano carbon, ZnO-Al_2O_3, and Ni-CeO_2 have shown a very high current, much more than that for platinum (Pt). So it is a very good achievement of producing a non-Pt based inexpensive high energetic electro catalytic materials. The computed maximum current delivered for these electrodes is given in the table 3 and the same is also given for Pt for comparison. It is seen that the maximum current is in the order of 30-60 mA/cm^2, which is a very good performance. That is a fuel cell fabricated with these developed materials of say 100 cm^2 surface area is expected to deliver a cell current of 3-6 amp from renewable biofuel.

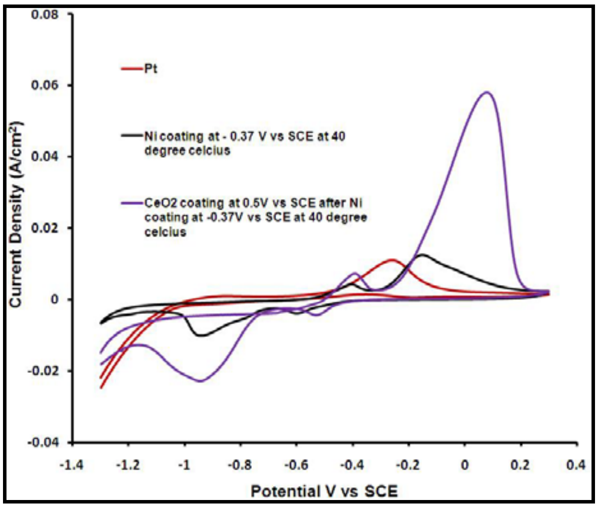

Fig.3.a. Cyclic Voltammetry of Ni-CeO_2 coated Cu foil and Pt in 1M ethanol + 1M KOH solution

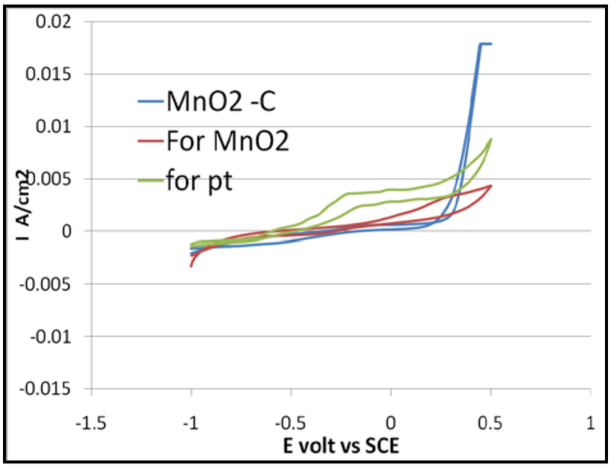

Fig.3.b. Cyclic Voltammetry of Pt, MnO_2 and MnO_2-C coated stainless steel electrodes in 0.5M glucose + 1M KOH solution.

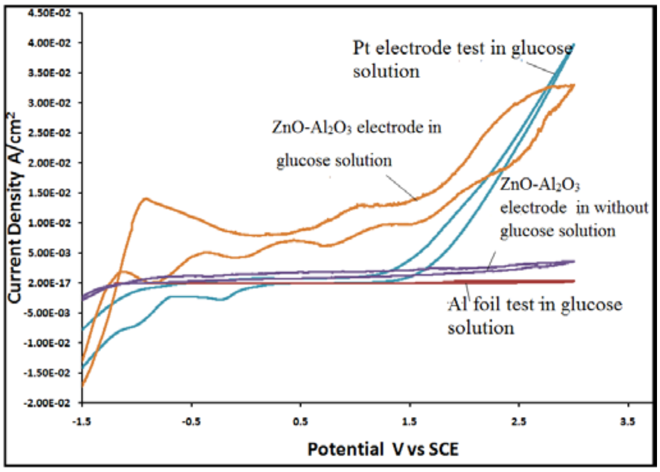

Fig.3.c. Cyclic Voltammetry of Pt, ZnO-Al_2O_3 coated and pure Al foil electrodes in 0.5M glucose solution in phosphate buffer solution

Table 3. Maximum Current delivers per unit area of different electro synthesized electrode materials in different solution in compares to Pt

Electrodes	**Maximum Current delivers per unit area (Imax) (mA/cm^2)**
Ni-CeO_2 -Cu in ethanol solution	57.8
Pt in ethanol solution	10.9
ZnO-Al_2O_3 in glucose phosphate buffer solution	32.6
Pt in glucose phosphate buffer solution	39.1
MnO2-C in glucose KOH solution	8
Pt in glucose KOH solution	17

3.3. *Chronoamperometry (CA):*

Having obtained high current peak in the CV study for electro coated materials; it is worthwhile investigating Chronoamperometry to find out the nature of steady state current. CA test was carried out at different fixed potential to find a potential where it gives steady higher current. Fig. 4.(a-c) shows CA study for Ni-CeO_2, MnO_2, MnO_2-C and ZnO-Al_2O_3 for their respective solutions at the fixed potential where it delivers steady higher current. It is seen that for all the curves, the current decreases with time initially till a steady state current is reached. The steady state current varies with different selected fixed potential at which oxidation of the fuel (glucose, ethanol, Methanol) takes place with release of electron which is basically the measured current. The potential at which the electrochemical oxidation of fuel takes place is a function of reversible potential, concentration of the reacting species, anodic and cathodic over voltages on the electrodes surfaces. That is why, depending upon the system and an overvoltage of the particular electro-catalytic surfaces, current peak occurs at a fixed potential. Thus it confirms that the inexpensive material, the electro-catalytic MnO_2-C, ZnO-Al_2O_3 Ni-CeO_2-Cu deliver a higher current compared to that of expensive Pt as far as glucose oxidation, ethanol oxidation are concerned.

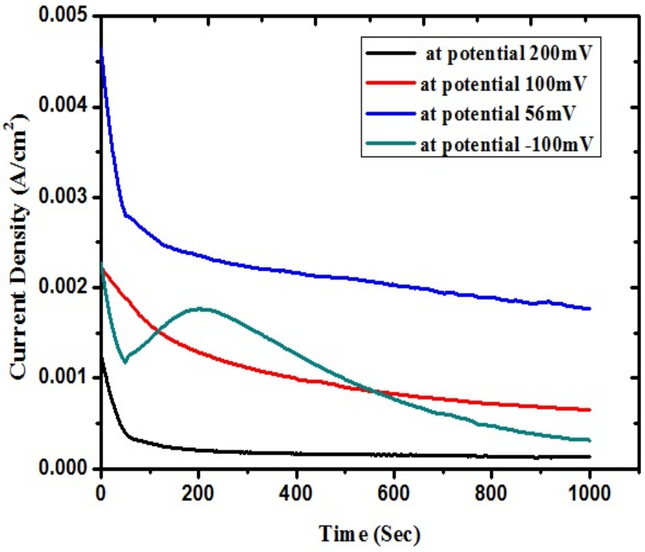

Fig.4.a. Variation of Current with time for Ni-CeO_2 coated Cu foil in 1M ethanol+ 1M KOH solution at different constant potential.

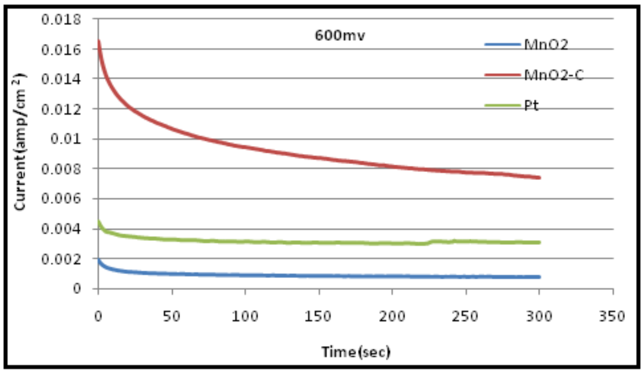

Fig.4.b. Variation of Current with time for MnO_2-C and MnO_2 coated SS304, Pt and in 0.5M glucose in 1M KOH solution with a constant potential 600mv Vs. SCE.

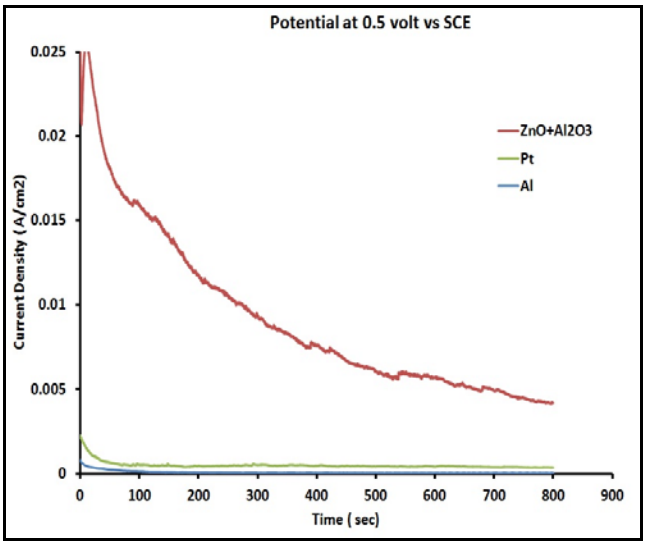

Fig.4.c. Variation of Current with time for ZnO-Al_2O_3, Al foil and Pt in 0.5M glucose in phosphate buffer solution with a constant potential 0.5V Vs. SCE

3.4. Material Characterization:

For better understanding of the constituents and the morphology the electrodeposited electrodes, materials characterization such as XRD and SEM are needful and explained in this section.

3.4.1. XRD:

Figures 5 (a-d) exhibits XRD of electro coated materials. The presence of Ni-Fe-Co-Al, Ni-CeO_2-Cu, MnO2-carbon and ZnO-Al_2O_3 are indicated by peak intensity in the figures. This confirms that by electro coating of Ni-Fe-Co-Al, MnO_2-carbon, ZnO-Al_2O_3 and Ni-CeO_2-Cu have been achieved and the good electro catalytic properties of the present investigated materials are due to the presence of these constituents.

3.4.2. SEM study:

Figures 6a, 6b, 6c, 6d display the morphology of SEM images of different electro synthesized Ni-Fe-Co, Ni-CeO_2, MnO_2-C, ZnO-Al_2O_3 materials respectively. The morphology of the deposited materials exhibits that there are channels or recess in between the grains (specially for fig 6 b & c). The grains are fine from with some in 100nm range. The fact accounts for more effective electrode surface area more charge-discharge current, giving rise to enhanced current (fig. 3 & table 3) . So actual 3D surface area is more than geometrical 2D planner area, for electrochemical oxidation of the fuel in fuel cell. The electrode substrate also shows sweep steps (up & down). This has enhanced the exchange current density (table-2).

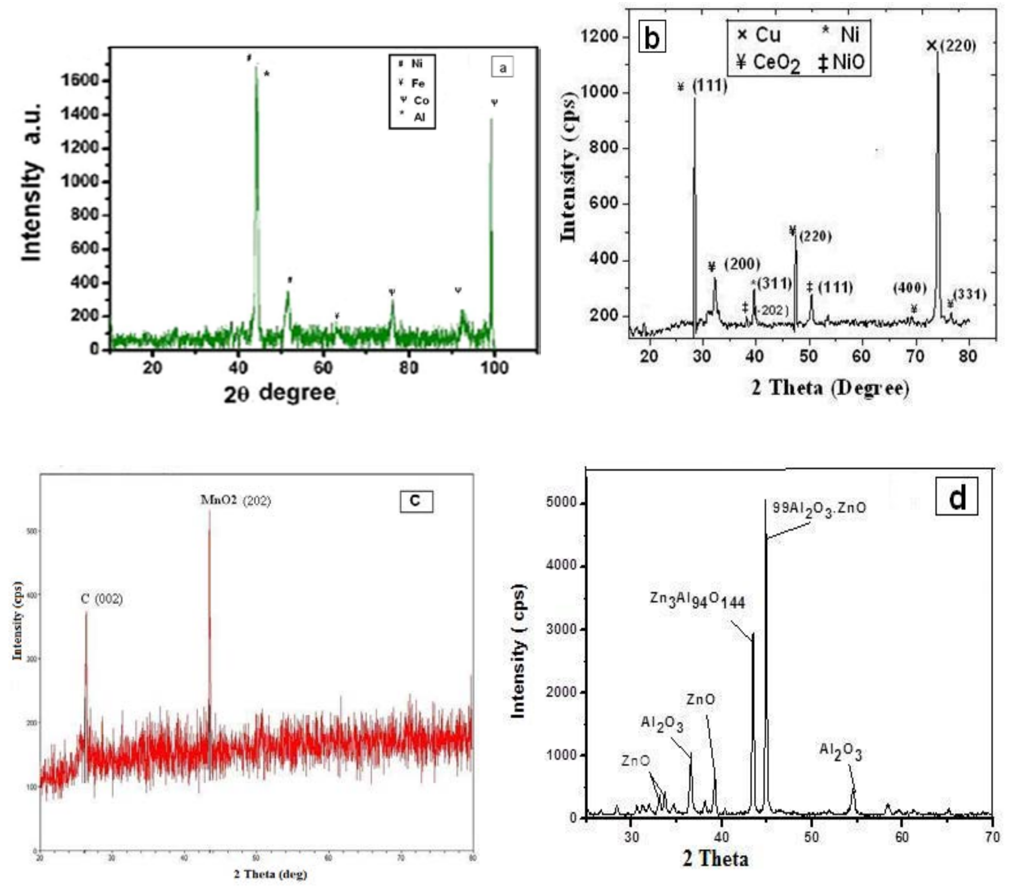

Fig.5. (a-d). XRD patterns of different electro synthesized materials, (a) XRD patterns of Ni-Fe-Co electrodeposited on Al-foil, (b) XRD patterns of Ni-CeO_2 electrodeposited on Cu foil. (c) XRD patterns of MnO_2-C deposited on SS304, (d) XRD patterns of ZnO-Al_2O_3 deposited on Al foil

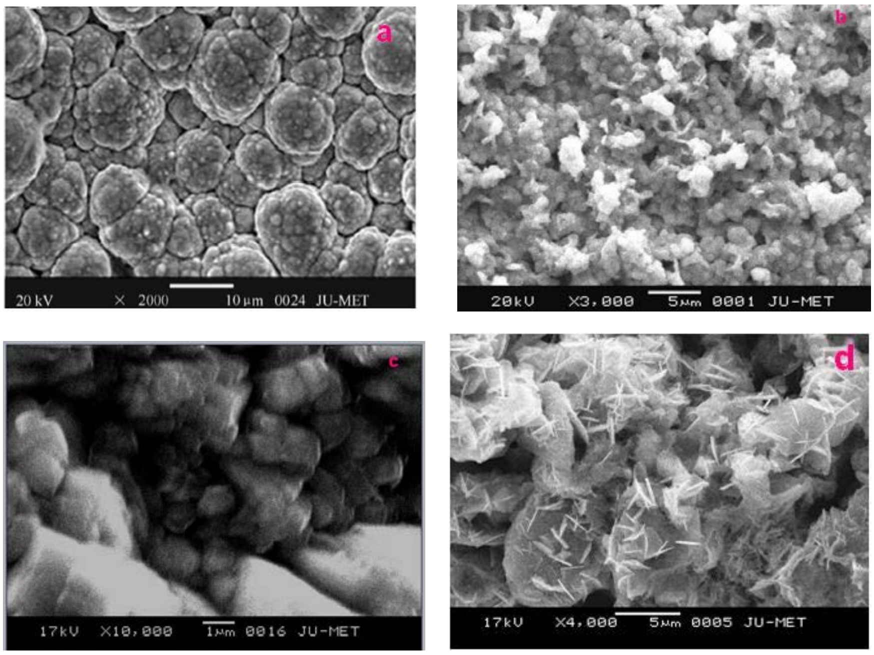

Fig. 6 (a-d). SEM micrographs of different electro synthesized materials.(a) Ni-Fe-Co electrodeposited on Al substrate (b) Ni-CeO_2 electrodeposited on Cu foil. (c) MnO_2-C deposited on SS304 (d) ZnO-Al_2O_3 deposited on Al foil

4. Summary

The results and discussions cited above throw some light on progress of Fuel Cell from laboratory scale to commercial scale and renewable energy synthesis can be achievable at an economically viable rate. The present investigation shows three inexpensive electrodes Ni-Co-Fe, MnO_2-C, ZnO-Al_2O_3, and Ni-CeO_2 which have a very good electrocatalytic property to electro oxidation of fuels such as ethanol and glucose, giving rise to a very high current in the order of 30 -60 mA/cm^2. The overvoltages of these electrodes are also very less so that the energy loss due to polarization is the minimum. The various electrochemical characterizations performed show the materials are even superior to Pt which is invariably used for fuel cell electrode for laboratory purpose but cannot be commercialized due to its high cost. The material characterization by XRD and SEM confirm that electrodes are alloys or oxide composite. The structure is micro to nano grains with recess or channel in between that accounts for high current obtained on electro oxidation of the fuel. The current delivered from the fuel cell for an electro surface areas about 100cm^2 is expected to be 5-6 amperes which is very encouraging outcome for the scientists, engineers and fuel cell manufacturer to move one scale up to manufacturing fuel cell unit at low cost.

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