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Synthesis and characterization of ZnO-Al₂O₃ oxides as energetic electro-catalytic material for glucose fuel cell

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Abstract: One of the thrust areas of research is to find an alternative fuel to meet the increasing demand for energy. Glucose is a good source of alternative fuel for clean energy and is easily available in abundance from both naturally occurring plants and industrial processes. Electrochemical oxidation of glucose in fuel cell requires high electro-catalytic surface of the electrode to produce the clean electrical energy with minimum energy losses in the cell. Pt and Pt based alloys exhibit high electro-catalytic properties but they are expensive. For energy synthesis at economically cheap price, non Pt based inexpensive high electro catalytic material is required. Electro synthesized ZnO-Al₂O₃ composite is found to exhibit high electro-catalytic properties for glucose oxidation. The Cyclic Voltammetry and Chronoamperometry curves reflect that the material is very much comparable to Pt as far as the maximum current and the steady state current delivered from the glucose oxidation are concerned. XRD image confirms the mixed oxide composite. SEM images morphology show increased 3D surface areas at higher magnification. This attributed high current delivered from electrochemical oxidation of glucose on this electrode surface.

Keywords: glucose; energy materials; electro-catalyst; cyclic voltammetry; chronoamperometry; polarization

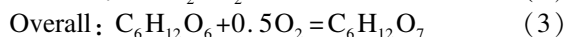
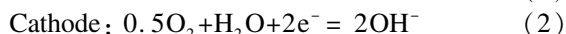
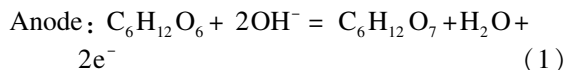
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One of most important challenges for today's scientists and engineers is to find a technology to produce pollution free energy from alternative fuels. With fast urbanization, advent of high tech cities and high quality life style, the demand for energy is increasing exponentially. But the reserve for quality fossil fuels is diminishing. Academicians and researchers, worldwide, are investing for other resources of energy producing biomass. Hydrogen is a clean fuel to produce energy through the electrochemical oxidation of a fuel, in a fuel cell. Paul et al^[1] produced hydrogen from green algae and used in fuel cell to synthesize clean electrical energy. Agriculture waste in the form rice husk or woody biomass is also a good alternative fuel resource to synthesize clean energy^[2-4]. Glucose is a good source of alternative fuel for clean energy. It is easily available, cheap and non-toxic bio-fuel. It is produced in abundance from both naturally occurring plants and industrial processes.

A fuel cell produces clean energy from the fuel with high energy efficiency by converting the fuel electrochemically directly to electrical energy, bypassing the limitation of Carnot cycle, which limits the high efficiency energy conversion. Thus energy synthesis through fuel developments with different bio-fuels is the thrust areas of research for the useful clean energy to meet the global growing demand of

pollution free renewable energy. Since the fuel in the fuel cell is electrochemically oxidized at anode, a high electro catalytic anode material needs to be developed to deliver a high current and hence energy from the cell. A good electro catalytic material has high exchange current density, low polarization resistance and kinetically produces a faster electron transfer to the anode from the electrochemical oxidation of the fuel.

Since the fuel is electro oxidized at anode, releasing electrons at it which conducts them towards cathode through an external load. In a glucose-based bio-fuel cell, the glucose is oxidized at the anode, while oxygen is reduced to water at the cathode. The nature of the electro catalytic property of the anode determines the rate of glucose oxidation. The associated oxidation products^[5] for glucose oxidation are shown below:



$$\Delta G^0 = -2.52 \times 10^6 \text{ J/mol}, E_0 = 1.30 \text{ V}$$

Rao et al^[6] reported that the gluconic acid was the only reaction product as identified by thin layer chromatography in phosphate buffer solution (pH value 7.4). Rao et al^[5] showed that the oxidation of glucose to gluconic acid yields only two

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electrons per molecule glucose. That is the glucose molecule is partly oxidized as shown in the equations above.

Direct glucose fuel cell (DGFC) is one of the best alternative sources of clean energy for today's scenario as it is easily available, nontoxic and non-flammable. Complete oxidation of glucose would have produced much more energy (2.87×10^6 J/mol) than that its partial oxidation. Finally glucose fuel cell operates at low temperature and hence can be easily used in portable devices etc.^[5,7,8]. The open circuit potential of DGFC cell is 1.24 V. In medical applications, glucose fuel cell in phosphate buffer solution is an important major researchable area^[9]. Considering all these aspects, the development of high electro catalytic energy material for the highest possible rate of glucose oxidation at anode is a major issue for developing DGFC.

Besides the electro catalytic properties of the electrode materials, the chemistry of the fuel and the electrolyte (constituents, pH value, temperature, etc)^[10-15] influences the output current and potential due to polarization factors. More interestingly the oxidation rate of the glucose is much higher in alkaline medium than the acidic or neutral pH value^[8,16]. Precious metals and their alloys, such as platinum (Pt) and gold (Au), are used as a catalytic electrode surface for glucose oxidation for last few decades. However, Pt is extremely susceptible to poisoning by CO and halides, and it is also very costly^[17,18]. CO poisoning effect of Pt had been attempted to minimize by adding of various co-catalysts, such as Ru, Sn, Au, W, Mo, Os, Re, Rh, Pd, Pb and Bi, to Pt^[18-21]. Platinum-based nano materials with high surface areas have been receiving increased attention due to their unique properties and a number of impressive applications in catalysis and fuel cells. Paul^[4] reported that aluminium electro coated with Pt, Pt-Ru and Pt-Ru-C for alcoholic fuel cell, produced high current of 15 ~ 25 mA/cm² and high power density of 10 ~ 15 mW/cm². Li et al^[22] synthesised gold nano particles supported on MnO₂-carbon nano composite (Au/MnO₂-C) for the anodic oxidation of glucose in a direct glucose alkaline fuel cell (DGAFC). They reported that the maximum power density of the fuel cell at 30 °C with an air cathode, using Au/MnO₂-C catalyst, is 1.1 mW/cm². This power density is higher than that of the commercial Au/C catalyst with half of the gold loading. On the other hand, Paul et al^[23] produced economically viable clean electrical energy through fuel cell, using MnO₂ as an electrode

material than conventional based electrode from the oxidation of alcoholic fuels. Slaughter et al^[24] fabricated Al/Au/ZnO abiotic catalyst by hydrothermal and dip-coating techniques for the development of an abiotically catalysed glucose fuel cell at pH value 7.4. They reported that, Al/Au/ZnO-Pt glucose fuel cell delivered a power density of 16.2 mW/cm² and a current density of 111.1 mA/cm². Among the non Pt based cheap, electro catalyst materials for fuel cell electrodes, transition metal sulphide and oxides^[25,26] have been proposed as alternatives to replace Pt. ZnO, a semiconductor with a band gap of 3.37 eV has attracted considerable attention in solar cells, optics and photonics due to its interesting properties, but the use of this material as support for electro catalyst has been not very much explored till now.

In this present investigation a new non platinum electro catalytic material ZnO-Al₂O₃ mixed oxide composite was synthesized by electro deposition. The electro catalytic properties of the synthesized composite oxides were carried out by cyclic voltammetric (CV), chronoamperometry (CA), and potentiodynamic test. The structural characterization of the synthesized material was done by X-ray diffraction (XRD) and scanning electron microscope (SEM).

1 Experimental

1.1 Material pre-treatment

Al-foil with the surface area of (1.5 × 1.5) cm² was 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. After that it is dried in hot air.

1.2 Electro synthesis of ZnO-Al₂O₃ oxide

Electro deposition of ZnO-Al₂O₃ on pre-treated Al-foil was carried out using a Potentiostat. The electrolyte was 0.5 mol/L ZnCl₂ aqueous solution bubbling with air and 0.2 mol/L KCl aqueous solution is added to increase the conductivity of the solution. A series of experiments was done at different temperature, varying current density and deposition time and pH value. The electro-deposition potential was controlled at -1.4 V (vs SCE) using HY3002 Potentiostat. The optimum conditions for electro-deposition have been found out and tabulated in Table 1.

1.3 Electrochemical characterization

The performance of the developed electro catalytic ZnO-Al₂O₃ oxide coated sample was

performed in glucose solution in phosphate buffer ($\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$) at pH value 7.4 by CV, CA, and potentiodynamic polarization tests.

Table 1 Electro deposition parameters for deposition of ZnO-Al₂O₃ oxide

Parameter	Range	Optimum
Current density $I/(\text{mA}\cdot\text{cm}^{-2})$	160 ~ 100	150
Time t/s	300 ~ 90	240
Temperature $t/^\circ\text{C}$	22 ~ 70	40
pH value	4 ~ 8	5

1.4 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.

1.5 Chronoamperometry (CA)

Chronoamperometry (CA) was tested in the same machine with different software. Experiment was carried out at different fixed potentials selected around the range of glucose oxidation potential as shown in equation (1) above. 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.

1.6 Polarization test

Potentiodynamic polarization test was conducted with three electrode system as stated above and the electro kinetic parameters R_p , I_0 , β_a , β_c were determined from polarization curve.

1.7 Physical characterization

X-ray diffraction (XRD) 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 $\text{Cu K}\alpha$ radiation at room temperature. The scan region (2θ) was varied from 25° to 75° at a scan rate of $2(^\circ)/\text{min}$. 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.

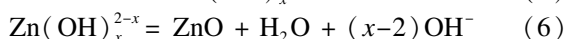
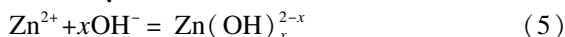
SEM Micrographs of the investigated samples were photographed using JEOL-JSM 6360 scanning electron microscope (SEM) at different magnification and high resolution.

2 Results and discussion

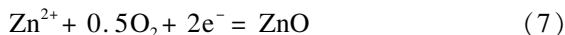
The synthesis of ZnO and Al_2O_3 composite was electro deposited in a galvanostatic circuit at an optimum condition in ZnCl_2 solution. ZnO- Al_2O_3 oxide is formed at cathode by these possible following reactions discussed here. It is known that water reduction potential is much nobler than that the Zinc electro deposition. Water reduction takes place with the formation of OH^- ion as follows.



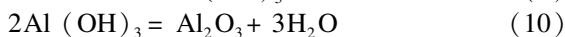
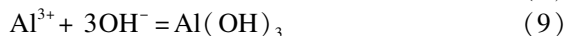
Zn^{2+} ions in the electrolyte will react with OH^- ions to form metal hydroxide. This metal hydroxide then further dissociates to more stable ZnO at temperature above 35°C [27,28]. The reactions are shown below:



Overall reaction can be written as



The proposed mechanism for the formation of Al_2O_3 oxide is given here. At the time of electro deposition, aluminium goes into solution through the dissolutions of ZnCl_2 . Al^{3+} ions readily combine with OH^- ion to form aluminium hydroxide. This hydroxide decomposes to Al_2O_3 oxide through the following reactions.



The electro-catalytic properties of the above electro synthesized composite oxide are discussed in the following sections.

2.1 Cyclic voltammetric (CV)

The CV results are shown in Figure 1. It is clearly seen in Figure 1 that both Pt and ZnO- Al_2O_3 oxide show the current peaks at a particular potential whereas there is no such peak for pure Al. So Pt and ZnO- Al_2O_3 are found to be good electro catalytic material for glucose oxidation. However, the current from the Pt substrate is more than that from ZnO- Al_2O_3 surface. It is interesting to note that CV for mere phosphate buffer electrolyte without glucose addition does not show any appreciable peak current. This proves that the current peak is due to glucose oxidation only.

2.2 Chronoamperometry (CA)

Figure 2 (a ~ d) exhibits CA study of the above three investigated material at different fixed potentials, i. e. -0.4 , 0.5 , 1.2 , 1.7 V vs saturated calomel electrode (SCE). It is seen for all the curves, the current decreases with time initially till a steady state current is reached. The steady state

current on ZnO-Al₂O₃ electro-catalytic surface is found to always more than that of Pt surface. The steady state current varies with different selected fixed potential at which oxidation of glucose 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, E^0 (reaction (1) ~ (3)), 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 ZnO-Al₂O₃ delivers a higher current compare to that of expensive Pt as far as glucose oxidation is concerned.

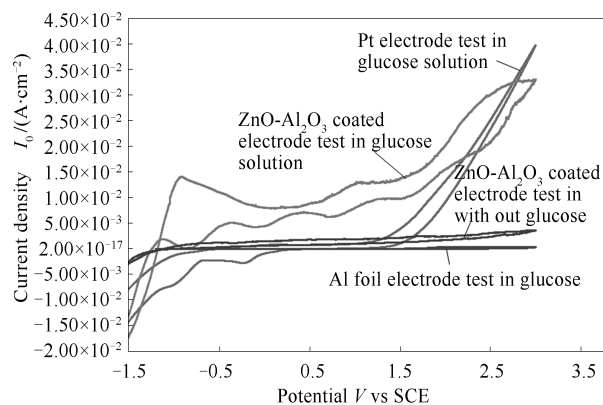


Figure 1 Cyclic voltammetry of Pt, ZnO-Al₂O₃ coated and pure Al foil electrodes in 0.5 mol/L glucose solution in phosphate buffer solution

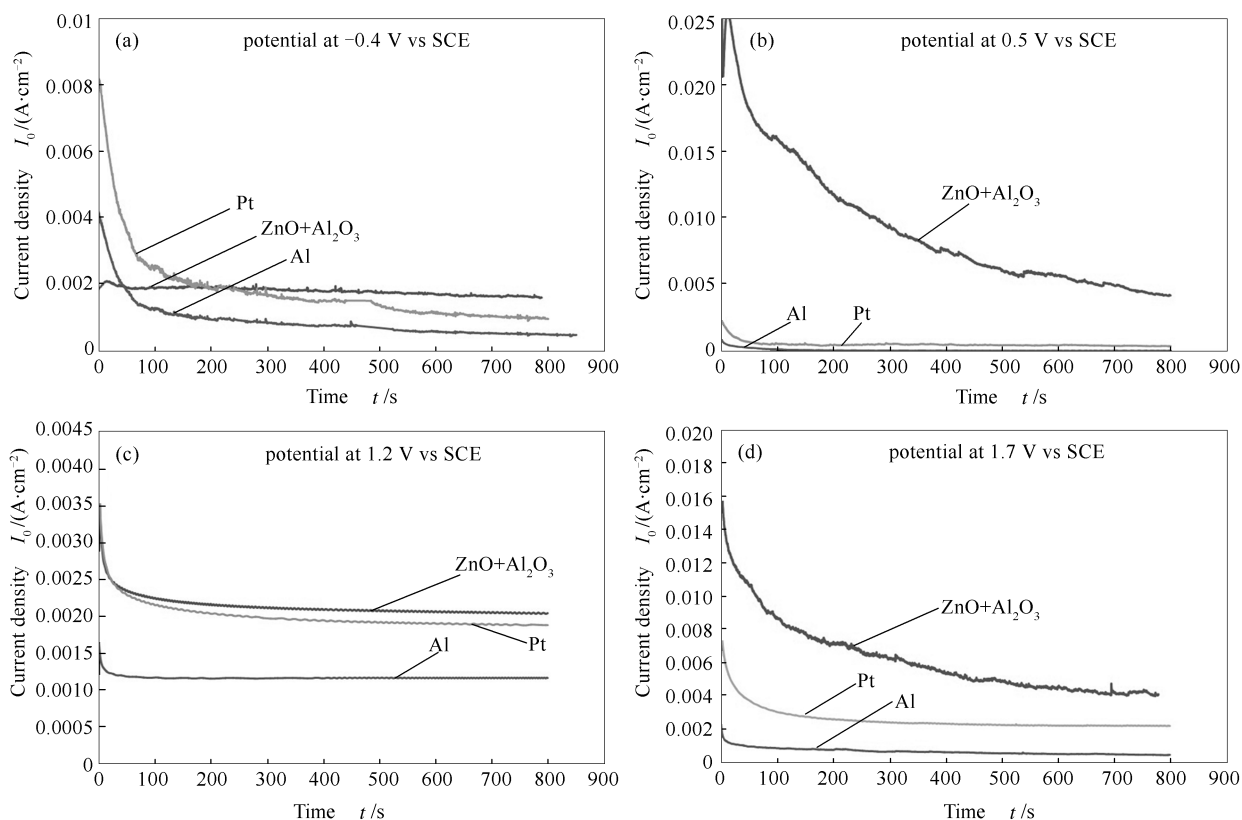


Figure 2 Variation of current with time for 0.5 mol/L glucose in phosphate buffer solution with different constant potential for different electrode materials
(a): -0.4 V; (b): 0.5 V; (c) 1.2 V; (d): 1.7 V

2.3 Polarization studies

Figure 3 depicts the polarization studies of the all types of electrodes in phosphate buffer glucose solution. It is seen that the curves for Pt and ZnO-Al₂O₃ are shifted to the right compared to the bare aluminium foil substrate. This means the current at which reversible reaction is occurring is higher for Pt and ZnO-Al₂O₃ compared to that on bare aluminium

substrate. The electro kinetic data computed from this Potentiodynamic curve (Figure 3) are illustrated in the Table 2. The electro-kinetic data i. e. polarization resistance (R_p) and exchange current density (I_0) computed from the Potentiodynamic curve (Figure 3) are graphically displayed in Figure 4 and Figure 5. It is interesting to find that the polarization resistance (R_p) is less for Pt and ZnO-Al₂O₃ surface compared to that

for bare aluminium surface. This shows that the resistance to flow of current becomes lower on a high electro-catalytic surface. Exchange current density which is a fundamental property of electro-catalytic surface and decides how fast a half cell reaction takes place at reversible potential, has been also computed

and shown in Figure 5. It is very encouraging to find the electro synthesized ZnO-Al₂O₃ oxide gives the highest current density for glucose oxidation. This confirms that the composite ZnO-Al₂O₃ oxide is superior to Pt as an electro catalytic energy mater as far as glucose oxidation is concerned.

Table 2 Electrochemical kinetic data of Al-foil, Pt and ZnO+Al₂O₃ coated substrate

Electro-catalytic material	β_c/V	β_a/V	Polarization resistance R_p/Ω	Exchange current density $I_0/(A \cdot cm^{-2})$
Al foil	0.15	0.12	2.5026×10^{-3}	0.98
Pt	0.19	0.25	3.0204×10^{-4}	8.139
ZnO+Al ₂ O ₃ coated material	0.10	0.16	2.4618×10^{-4}	9.987

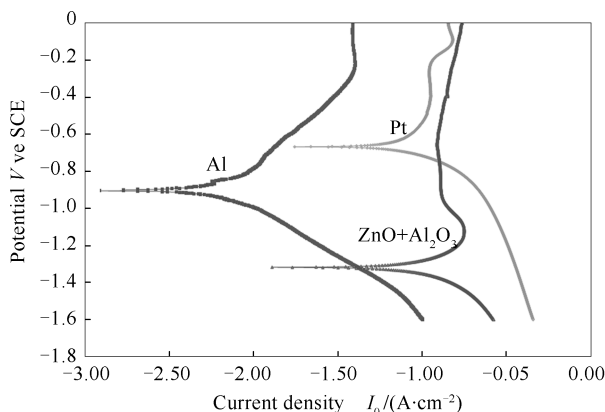


Figure 3 Polarization study of Pt, ZnO-Al₂O₃ coated and pure Al foil electrodes in 0.5 mol/L glucose solution in phosphate buffer solution

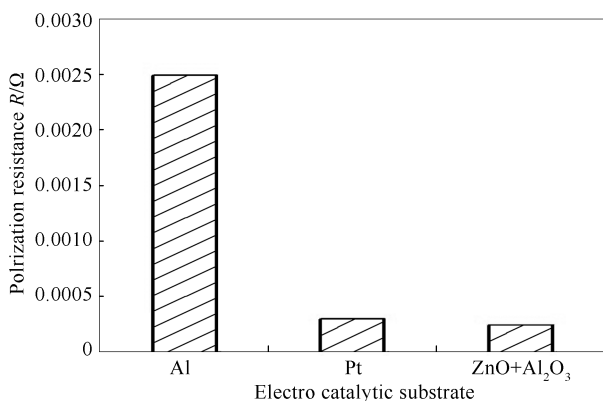


Figure 4 Comparison of polarization resistance of Pt, ZnO-Al₂O₃ coated and pure Al foil electrodes in 0.5 mol/L glucose solution in phosphate buffer solution

2.4 XRD

The XRD of the synthesized ZnO-Al₂O₃ composite is shown in Figure 6. It shows peaks of pure ZnO and Al₂O₃ as well as composite forms of ZnO-Al₂O₃ and Zn₃Al₉₄O₁₄₄ at different 2θ (Brag angle). The peak intensity is the highest for ZnO-Al₂O₃ composite followed by a compound Zn₃Al₉₄O₁₄₄. So the results clearly indicates that the

electro deposited material consist of few mixed oxides of semiconductor mostly composite of ZnO-Al₂O₃ with few spots of pure oxides. It is thought that the high current density produced from the electrode surface is due to this composite of ZnO-Al₂O₃ and Zn₃Al₉₄O₁₄₄.

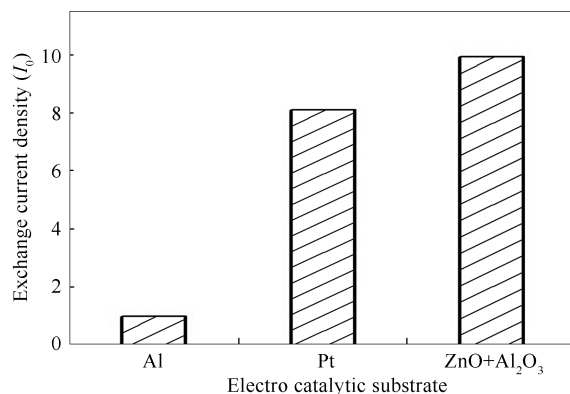


Figure 5 Comparison of exchange current density of Pt, ZnO-Al₂O₃ coated and pure Al foil electrodes in 0.5 mol/L glucose solution in phosphate buffer solution

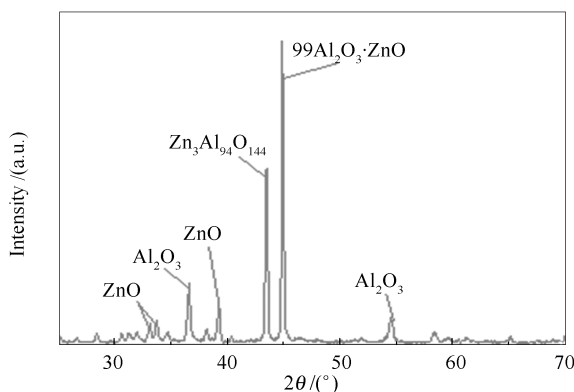


Figure 6 XRD patterns of ZnO-Al₂O₃ mixed oxide coated sample

2.5 SEM micrographs

Figures 7 (a), 7 (b), 7 (c) display the morphology of SEM images of the coated ZnO-Al₂O₃ oxide at three different magnifications, i. e. 500 ×,

1 000 × and 4 000 ×. The SEM structure looks like honeycomb structure with inner pores. It is clearly revealed that the oxide surface is not a plane but a 3D morphology with pores and sub-surface which makes a much more enhanced electrode surface area than what

is determined by planer geometry of a length and breadth. This enhanced surface area is the key to increase in current as obtained in Figure 1 and also high exchange current density as found in Figure 5.

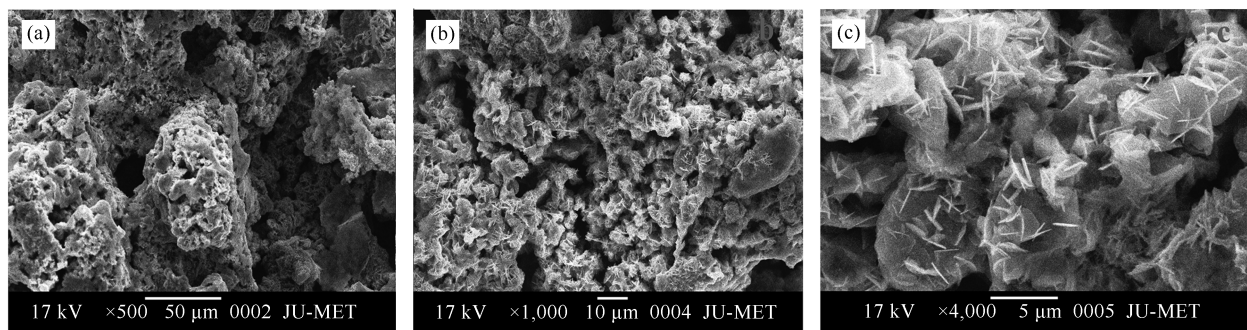


Figure 7 SEM micrographs of the oxide coated sample at different magnification
(a) : ×500; (b) : ×1 000; (c) : ×4 000

3 Conclusions

Electro synthesized ZnO-Al₂O₃ oxide exhibits very good electro-catalytic properties comparable to those of Pt for glucose oxidation as found by different electrochemical studies. This inorganic oxide coated electrode is very much inexpensive compared to Pt and its alloys which are invariably used as fuel cell electrode. The present investigation opens up an area

of further investigation of fabricating low temperature glucose fuel cell using this present investigative inexpensive high energetic material to produce clean energy from an alternative fuel such glucose at a much cheaper rate.

Acknowledgement

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