

文章编号: 0253-2409(2015)03-0344-08

## Electrochemical characterization of MnO<sub>2</sub> as electrocatalytic energy material for fuel cell electrode

Subir Paul, Asmita Ghosh

(Department of Metallurgical and Material Engineering, Jadavpur University, Kolkata 700032, India)

**Abstract:** Development of inexpensive non Pt based high electrocatalytic energy materials is the need of the hour for fuel cell electrode to produce clean alternative green energy from synthesized bio alcohol using biomass. MnO<sub>2</sub>, electro synthesized at different current density is found to be well performed electrocatalytic material, comparable to Pt, with higher current density, very low overvoltage for the electrochemical oxidation of methanol. From EIS study, the polarization resistance of the coated MnO<sub>2</sub> is found to be much low and electrical double layer capacitance is high, the effect increases with increase in current density of electro deposition. XRD, EDX and AAS analysis confirm the MnO<sub>2</sub> deposition. The morphology of SEM images exhibits an enhanced 3D effective substrate area, for electro oxidation of the fuel. A few nano structured grains of the deposited MnO<sub>2</sub> is also observed at higher current density. The fact supports that a high energetic inexpensive electro catalytic material has been found for fuel cell electrode to synthesis renewable energy from methanol fuel.

**Keywords:** electro catalytic; energy material; fuel cell impedance; polarization; electro coating

**CLC number:** O646      **Document code:** A

A fuel cell produces clean energy from the fuel with high efficiency by converting the fuel electrochemically, directly to electrical energy, bypassing the limitation of Carnot cycle, which limits the high efficiency energy conversion. The fuel used in the fuel cell may be generated from the different sources of biomass. Development of fuel cell using the derived fuel from the biomass<sup>[1-4]</sup> will be the most useful clean energy synthesis from alternative fuel to meet the global growing demand of pollution free renewable energy. Extensive works are being carried out to produce biofuels from different sources of biomass. H<sub>2</sub> produced from the fresh water green algae was directly used in fuel cell to produce a cell potential in the range of 300 ~ 600 mV<sup>[1]</sup>. Agriculture wastes generate a huge amount of woody biomass, which can be converted to alternate fuel like bio oil<sup>[2]</sup> or to ethanol by hydrolysis and subsequent fermentation by microorganism<sup>[3-7]</sup>. Direct methanol and ethanol fuel cells are the most extensively researched as these fuels can easily be produced from biomass. Since the fuel in the fuel cell is electrochemically oxidized at the anode and the output current is delivered at the cathode, the materials and surface properties of the anode and cathode are the most important part of all activities of the fuel cell development. The electrocatalytic properties of the electrode surface such as exchange current density, polarization resistance and electrochemical impedance need to be modified by surface treatments such as

coatings to make high electrocatalytic energy materials. A good electro catalytic surface produces faster electron transfer to the anode from the electrochemical oxidation of the fuel, or reduces cations at the cathode, delivering a high output current from the cell. Pt having very high exchange current density for many redox systems is invariably used for the laboratory scale fuel cell electrode. Being expensive, alternative and cheaper electrode materials with high electro catalytic property, need to be developed. The problems occurring with the electrode materials are the polarizations of the cathode and anode that hinder, the high output current and on load cell potential<sup>[3,4]</sup>. A good anode material should have the electro catalytic property for fast electrochemical oxidation of the fuel along with good electrical conductivity, low polarization resistance, strong biocompatibility, chemical stability and anti-corrosion property. Cathode materials on other hand should have capacity to capture and transfer electron rapidly with high redox potential, besides low polarization resistance. Both the materials need to have good strength and toughness. Carbon and metallic materials are normally being used for the anode and cathode. Due to its excellent electrical conductivity and chemical stability, the graphite rod has become one of the most commonly used electrodes in MFCs. However the output power was much larger when the graphite rod was replaced by graphite felt, indicating that increasing the surface area was beneficial to the

**Received date:** 2014-11-05; **Received in revised form:** 2015-01-20.

**Corresponding author:** Subir Paul; Tel&Fax: +91-33-2457-2185, E-mail: spaul@metal.jdpu.ac.in.

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)。

performance of the MFC<sup>[8]</sup>. Carbon paper and carbon cloth also act as good electrodes. The main benefit of them is the reduction in the distance between the two electrodes to improve the performance of the cell<sup>[9,10]</sup>.

Pt is an excellent catalyst for dehydrogenation but it is expensive and extremely susceptible to poisoning by CO and halides<sup>[11]</sup>. These remain strongly adsorbed on the Pt surface and block the active sites from further catalysis, resulting in a dramatic decrease in efficiency and overall performance. Efforts to minimize this poisoning have been centered around with the addition of co-catalysts such as Ru, Sn, Au, W, Mo, Os, Re, Rh, Pd, Pb, Bi and Ir to Pt to promote CO oxidation<sup>[12-15]</sup>. Platinum-based nanomaterials 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. In our previous work, nano porous anodized Al was electro coated with Pt, Pt-Ru and Pt-Ru-C were electrodeposited to produce Pt based nanomaterials electrodes for alcoholic fuel cell<sup>[4]</sup>. The cells produced high current of 15 ~ 25 mA/cm<sup>2</sup> and high power density of 10 ~ 15 mW/cm<sup>2</sup>.

Non Pt based electro catalysts are investigated for low cost fuel cell and being found to be good alternatives for Pt based electrodes. Several oxides and Ti alloys have been found to show good electro catalytic properties. Materials such as CoTMPP<sup>[16]</sup>, PbO<sub>2</sub><sup>[17]</sup>, TiO<sub>2</sub><sup>[18]</sup> show very encouraging results for application in fuel cell electrodes. There are a few works on Ni based alloy electrodes development for fuel cell. A small addition of Al to Ni produced an improved electrode property as cathode in molten carbonate fuel cells ( MCFC )<sup>[19]</sup>. A wide compositional range of Ni-Pd alloy catalysts were

prepared by Suresh Kumar for application as anode materials for methanol oxidative fuel cells in alkaline conditions<sup>[20]</sup>. Synthesis and characterization of Ni-Co and Ni-Co-Fe on Al by electrodeposition were also investigated by us<sup>[21]</sup>, for the development of low cost alcoholic fuel cell. The electrocatalytic surface properties of these coated alloy, viz. exchange current density, polarization resistance, electrochemical impedance are enhanced by tenths to hundreds order compared to those of bare Ni or Al surface.

There are a few works on MnO<sub>2</sub> based alloy electrodes development for fuel cell. Das et al<sup>[22]</sup> developed  $\beta$ -MnO<sub>2</sub> electrocatalytic material for carbohydrate oxidation.

In the present investigation attempts have been made to fabricate electrodes of electrodeposited MnO<sub>2</sub> on 304 stainless steel by electrodeposition and electrochemical characterization of these electrodes were made by polarization and electrochemical impedance spectroscopy. The surface morphology of the materials was examined by SEM and the structural characterization of the materials was examined by XRD.

## 1 Experimental

304 steel was used as substrate on which MnO<sub>2</sub> alloy was electrodeposited. The substrate was polished by 2/0 and 3/0 gradation emery papers. It was then rinsed in soap water and double distilled water.

The pretreated samples were electrodeposited in a solution of 0.34 mol/L MnSO<sub>4</sub> salt and 0.6 mol/L of H<sub>2</sub>SO<sub>4</sub> at 120 °C temperature and at different current densities viz. 50 mA/cm<sup>2</sup>, 100 mA/cm<sup>2</sup>, 150 mA/cm<sup>2</sup>, as shown in Table 1. The coated sample was rinsed by acetone and methanol one by one and then dried in an oven at 80 °C overnight.

**Table 1 Controlling parameters electro coating MnO<sub>2</sub>**

Substrate	Electrolyte chemistry	Current density $J / (\text{mA} \cdot \text{cm}^{-2})$	Time $t / \text{min}$	Temperature $t / ^\circ\text{C}$
304 steel	0.6 mol/L MnSO <sub>4</sub> +0.34 mol/L H <sub>2</sub> SO <sub>4</sub>	50	45	120
		100	-	-
		150	-	-

For polarization study, the anodic solution was 1 mol/L methanol and 0.5 mol/L H<sub>2</sub>SO<sub>4</sub>, purged by argon. The cathodic solution was 0.2 mol/L potassium ferricyanide in phosphate buffer (prepared by dissolving 4.08 g Na<sub>2</sub>HPO<sub>4</sub> and 3.29 g NaH<sub>2</sub>PO<sub>4</sub> in 500 mL water). The solution was purged by air using an air pump. Electrochemical measurements were conducted using a Gamry Potentiostat instrument coupled with Echem analyst software, controlled by a

personal computer, in a conventional three electrodes system cell. The cell consisted of MnO<sub>2</sub> coated, as working electrode, a graphite rod 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 the working electrode surface to minimize IR drop. A series of experiments with electrodeposited MnO<sub>2</sub> electrocatalysts, developed at

an optimum electroplating condition, were performed in anodic and cathodic solutions, to determine the various electrochemical parameters viz. exchange current density  $I_0$ , corrosion potential  $E_{\text{corr}}$ , corrosion current  $I_{\text{corr}}$ , the anodic and cathodic Tafel constants  $\beta_a$  and  $\beta_c$ . The potential was scanned between  $-1$  V and  $0.8$  V vs. SCE at a scan rate of  $1$  mV/s.

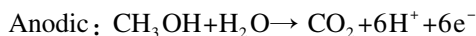
For EIS study, the experimental arrangement was same as that of polarization studies. The electrochemical cell was connected to an impedance analyzer (EIS300 controlled by Echem analyst software) for electrochemical impedance spectroscopy. The electrochemical impedance spectra were obtained at frequencies between  $100$  kHz and  $0.1$  Hz. The following results and information were obtained from the EIS experiments. Polarization resistance ( $R_p$ ), electrolyte resistance ( $R_u$ ), double layer capacitance ( $C_{\text{dl}}$ ), capacitive load or constant phase element (CPE ( $Y$ )), and  $\alpha$  which is defined from the capacitive impedance equation  $Z = 1/C(j\omega)^{-\alpha}$ . Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element (CPE). The exponent  $\alpha$  is 1 for ideal capacitance. For a constant phase element, the exponent  $\alpha$ , is less than one.

The X-ray diffraction technique is used to define the crystalline structure and the crystalline phases in the coated surfaces. This test was done using a Rigaku Ultima III X-ray diffractometer for recording the diffraction traces of the samples with monochromatized Cu  $K\alpha$  radiation, at room temperature, the scan region ( $2\theta$ ) was ranged from  $20^\circ$  to  $100^\circ$  at a scan rate of  $5(^\circ)/\text{min}$ .

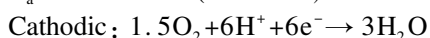
The electron micrographs were studied by SEM with accelerating voltage  $30$  kV, magnification up to  $300\,000\times$ . The images of the coated electrode samples were photographed at low and high magnification. The average elemental composition of the deposit was measured by means of an Energy-Dispersive X-ray (EDX) spectroscope attached to the SEM.

## 2 Results and discussion

The anodic and cathodic reactions in methanol fuel cell, with anodic solution (methanol solution under anaerobic condition) and cathodic solution (potassium ferricyanide in phosphate buffer) are given below.



$$E_a = -0.016 \text{ V (vs. SHE)} \quad (1)$$



$$E_c = 1.229 \text{ V (vs. SHE)} \quad (2)$$

$\text{H}^+$  generated during oxidation of alcohol gets diffused into cathodic chamber through the membrane

and supply  $\text{H}^+$  ions for cathodic reduction reaction of  $\text{O}_2$  to pure water. In order to estimate the performance of the electrodeposited electro catalysts, the following studies were performed.

### 2.1 Polarization studies of coated electrodes

Figure 1 displays the polarization of  $\text{MnO}_2$  samples coated at different current density, on 304 steel. It is seen that the polarization curves for the coated materials shift to the right in comparison to those for bare surface materials, which indicates that the coating of  $\text{MnO}_2$  produces higher current. There is not much noticeable difference of the curves when the current density of electrodeposition was increased from  $50$  to  $100$   $\text{mA}/\text{cm}^2$ . However at much higher current of  $150$   $\text{mA}/\text{cm}^2$ , a noticeable jump in current density is observed, indicating much better electrocatalytic  $\text{MnO}_2$  was formed. The effect of  $\text{MnO}_2$  coating on SS at different current density in cathodic solution is also reflected in Figure 2.

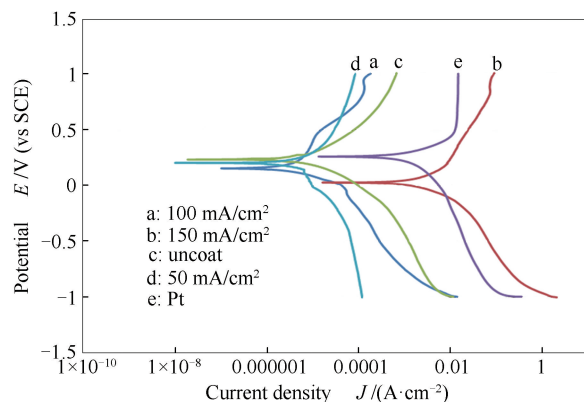


Figure 1 Polarization of curves of electro coated  $\text{MnO}_2$  at different current density, in methanol solution under anaerobic condition at  $25^\circ\text{C}$  (anodic solution), the same for 304 steel and Pt are given for comparison

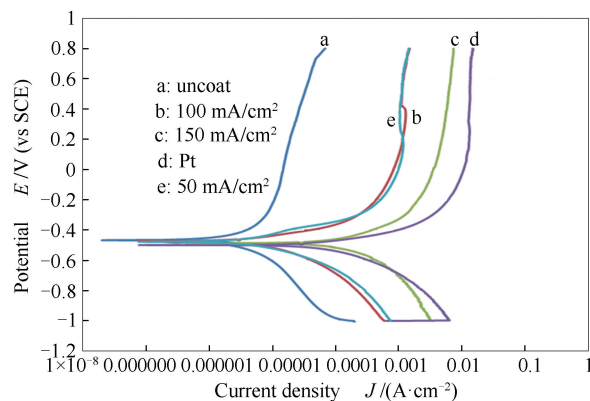


Figure 2 Polarization of curves of electro coated  $\text{MnO}_2$  at different current density in aerated phosphate buffer solution at  $25^\circ\text{C}$  (cathodic solution), the same for 304 steel and Pt are given for comparison

The curves of the coated surface shift towards right with increasing current density. It is very much clear from the comparative illustration of exchange current density in Figure 3, that the MnO<sub>2</sub> coating had tremendous effect on improving electro catalytic surface for application as electrodes in both anodic and cathodic compartments in alcoholic fuel cell. The various electrochemical parameters ( $\beta_a$ ,  $\beta_c$ ,  $E_{corr}$ ,  $I_{corr}$ ,  $I_o$ ) estimated from experimental data have been illustrated in Table 2. It is very interesting to note that

the value of  $I_o$  is increased by a few hundred times for MnO<sub>2</sub>, compared to those without coating, in both anodic and cathodic solution. The  $I_{corr}$  values have also been enhanced by coating. However the  $I_o$  value for Pt is the highest in both the solutions. It is also to be noted that the electrocatalytic properties ( $\beta_a$ ,  $\beta_c$ ,  $I_{corr}$ ,  $I_o$ ) of all the material are always better in anodic solution when methanol as fuel is electrochemically oxidized.

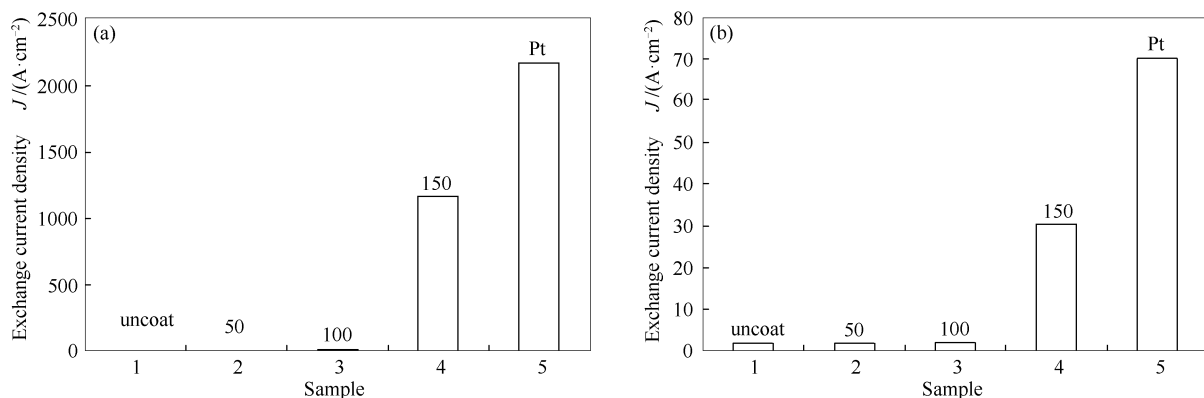


Figure 3 Comparison of exchange current density of electro coated MnO<sub>2</sub> at different current density, the same for 304 steel and Pt

(a) : anodic solution (anaerobic methanol solution) ; (b) : cathodic solution (aerated phosphate buffer solution)

**Table 2 Comparison studies of experimental computed electrochemical kinetic data of different coated metals and bare metal, in anodic solution and in cathodic solution**

Material	In anodic solution (anaerobic methanol solution)					In cathodic solution (phosphate buffer solution)				
	$\beta_a/mV$	$\beta_c/mV$	$I_{corr}/(\mu A \cdot cm^{-2})$	$E_{corr}/V$	$I_o/(\mu A \cdot cm^{-2})$	$\beta_a/mV$	$\beta_c/mV$	$I_{corr}/(\mu A \cdot cm^{-2})$	$E_{corr}/V$	$I_o/(\mu A \cdot cm^{-2})$
<sup>a</sup> 50 mA/cm <sup>2</sup>	115	133.4	98.8	0.238	2.17	289.6	168	91.8	-0.488	1.83
<sup>a</sup> 100 mA/cm <sup>2</sup>	196.7	198.2	58.3	0.120	20.4	372.5	176.8	65.8	-0.507	2.01
<sup>a</sup> 150 mA/cm <sup>2</sup>	341.8	408	42.8	0.071	1170	547	365	49.21	-0.516	30.5
Pt sample	356.3	455	40.9	0.253	2170	566	392	25.0	-0.526	70.5
Bare 304 SS	66.4	72.20	339.56	0.395	1.88	94.01	37.8	921	-0.378	1.72

a; MnO<sub>2</sub> coated at Cd

## 2. 2 EIS ( Electrochemical Impedance Spectroscopy)

EIS study was carried out for better understanding of the fundamental aspect of electrochemical phenomena at metal-electrolyte interface. The phenomena at the interface of the solid metal coated surface and aqueous electrolyte is a complex process consisting of line of positive and negatively charged ions, capacitance due to electrical double layer, coating or film formation on surfaces, polarization resistance ( $R_p$ ), pore resistance ( $R_{po}$ ) and various impedances due to diffusion of ions, movement of charge in or away from metal surface and adsorption of cation and anion. The whole phenomena can be represented by an equivalent AC

electrical circuit. The phenomena can be interpreted from Nyquist and Bode plots, which are depicted and discussed in the following section for various electro coated electrocatalysts. EIS has the great advantages over traditional DC electrochemical technique. The perturbation AC signal is very small and the resultant polarization of the electrode is in a linear potential region. Therefore there is no destructive damage to the electrode. EIS technique is used to evaluate the time relation interface parameter.

Figure 4 shows the Bode plots for MnO<sub>2</sub> coated electrode at different current density in anaerobic methanol solution. The curves show the characteristics of Randle circuit (inset in the Figure) of impedance vs frequency with missing values at very

low frequency. It is seen that the impedance values for alloy coated surface are drastically reduced with increasing current density. The phase angle of the coated electrodes (coated at a current density of  $150 \text{ mA/cm}^2$ ) is in the range of  $10 \sim 35$  degree, whereas for uncoated SS surface, it approaches close

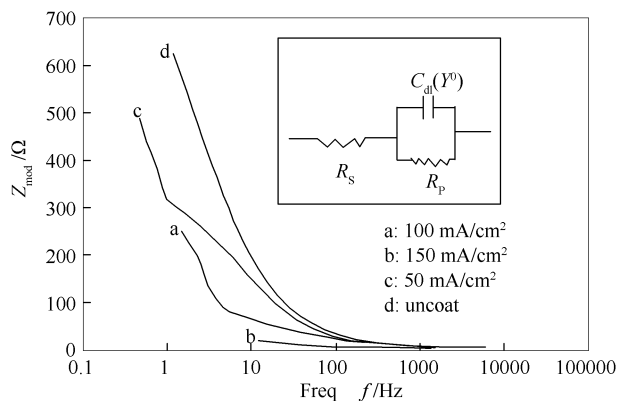
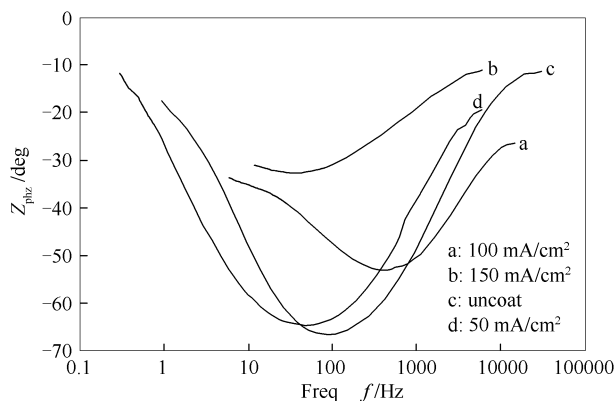


Figure 4 Bode plot electro coated  $\text{MnO}_2$  at different current density, in methanol solution under anaerobic condition at  $25^\circ\text{C}$  (anodic solution), the same for 304 steel and Pt are given for comparison

The Nyquist plots (Figure 5) of the same experimental data show that it is a semicircle for bare SS surface with  $Z_{\text{real}}$  value quite high compared to those of coated surface, indicating the high polarization resistance of the uncoated surface has been reduced a lot by  $\text{MnO}_2$  coating. The computed values of EIS parameter found by matching the Bode plots with an equivalent circuit close to Randle circuit, with  $C_d$  parallel to  $R_p$  are illustrated in Table 3. It is seen here that the polarization resistance  $R_p$  has been drastically reduced from 1 220 ohm to order of 4. 183 by  $\text{MnO}_2$  coating. However  $R_p$  is minimum for Pt. The constant phase element  $Y^0$  (behaving like capacitance) increases with increase in current density of  $\text{MnO}_2$  electrodeposition. Since reactance arising out of capacitance is the reciprocal of  $Y^0$ , an increase in it, leads to less polarization or resistive load and

to 70 degree. This indicates that the interface at the electrode-solution, behaves as pure capacitive load for uncoated SS and as a constant phase element (which deviates from an ideal capacitor), for the  $\text{MnO}_2$  coated SS. This makes the charge discharge reactions faster with a coating.



hence more flow of current. This produces a better electro catalytic energy material.

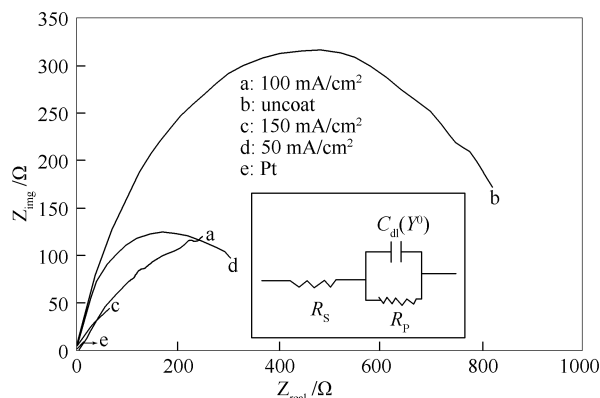


Figure 5 Nyquist plot electro coated  $\text{MnO}_2$  at different current density, in methanol solution under anaerobic condition at  $25^\circ\text{C}$  (anodic solution), the same for 304 steel and Pt are given for comparison

**Table 3 Comparison studies of experimental computed electrochemical impedance spectroscopy data of different coated samples and bare metal, in anodic solution and in cathodic solution**

Material	Anodic solution (anaerobic methanol solution)				Cathodic solution (phosphate buffer solution)			
	$R_p/\Omega$	$R_s/\Omega$	$Y^0(S * s^a)/\mu\text{F}$	$\alpha$	$R_p/\Omega$	$R_s/\Omega$	$Y^0(S * s^a)/\mu\text{F}$	$\alpha$
<sup>a</sup> 50 mA/cm <sup>2</sup>	299.1	4.802	61.87	0.272	913.3	18.96	$645.9 \times 10^{-3}$	0.179
<sup>a</sup> 100 mA/cm <sup>2</sup>	81.21	4.183	66.89	0.249	634.9	38.04	$700.6 \times 10^{-3}$	0.187
<sup>a</sup> 150 mA/cm <sup>2</sup>	31.36	2.462	82.46	0.179	156.3	42.34	$767.4 \times 10^{-3}$	0.176
Pt sample	26.63	3.703	109.83	0.125	126.5	75.47	$788.8 \times 10^{-3}$	0.103
Bare 304 SS	891	1220	4.222	0.388	$1.349 \times 10^3$	18.57	$496.5 \times 10^{-3}$	0.339

a:  $\text{MnO}_2$  coated at Cd

The  $Y^0$  value for Pt is however the highest, indicating it to be superior electro catalytic material.

Similar EIS studies are shown in Figure 6 (Bode plots) and Figure 7 (Nyquist plots). In this case

also, the same trend of lower impedance with higher current density of MnO<sub>2</sub> deposition is noticed (Figure 6). The phase angle vs. frequency curves are of similar nature (Figure 6), but the phase angle degree

for the bare surface is much more than the same for the coated surface, indicating the capacitive load at the interface has been decreased by the coating of MnO<sub>2</sub>.

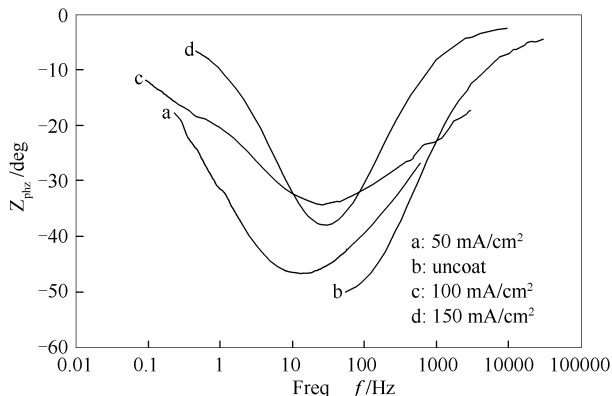
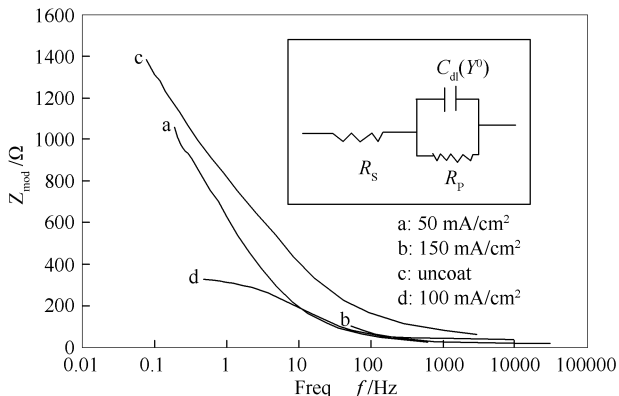


Figure 6 Bode plot of electro coated MnO<sub>2</sub> at different current density in aerated phosphate buffer solution at 25 °C (cathodic solution), the same for 304 steel and Pt are given for comparison

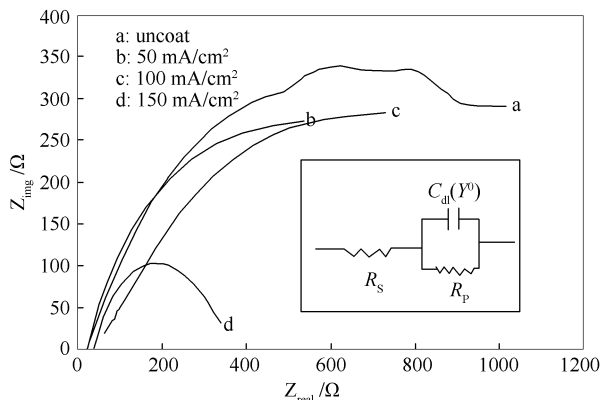


Figure 7 Nyquist plot of electro coated MnO<sub>2</sub> at different current density in aerated phosphate buffer solution at 25 °C (cathodic solution), the same for 304 steel and Pt are given for comparison

The EIS parameters computed from the data are illustrated in Table 3. It is seen from the table that baring Pt, the coated MnO<sub>2</sub> surface produces much lower R<sub>p</sub> and high Y<sup>0</sup>, with increasing current density. Thus from the foregoing EIS results, It is seen that MnO<sub>2</sub> coated on stainless steel, can act as very good electrocatalytic energy material electrode in both anodic and cathodic solutions in methanol fuel cell. And higher the current of electrodeposition of MnO<sub>2</sub>, better is the electro catalytic property, which is lower polarization resistance and higher capacitive load at the electrode/solution interface. This gives rise to low overvoltage for oxidation of methanol solution at the anode and also reduction of cations in cathodic solution at the cathode. Again α which signifies a deviation from pure capacitive load (Table 3), also distinguishes coated and uncoated electrodes

significantly. The double layer capacitance at the metal/solution interface behaves close to pure capacitance for uncoated SS and a constant phase element for coated surfaces, indicating faster charge transfer at the latter.

**2.3 XRD, EDX, AAS analysis**

The X-ray diffraction of the electrocoated MnO<sub>2</sub> (Figure 8) is indicated by peaks intensity at different 2θ values.

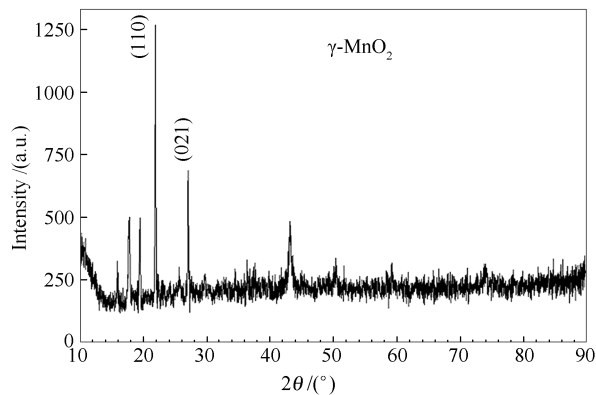


Figure 8 XRD patterns of coated MnO<sub>2</sub> sample at 100 mA/cm<sup>2</sup> current density

It is γ-MnO<sub>2</sub>. The bigger peaks are from (110) and (021) planes of γ-MnO<sub>2</sub>. The other smaller peaks are from the constituents (Fe, Cr, Ni) of the substrate, 304 steel (being not of interest in the present investigation, were not considered in the Figure). This confirms electro deposition of MnO<sub>2</sub> on 304 steel. The average elemental composition of different MnO<sub>2</sub> coated on 304 steel surface, at specific sites, during electron microscopy study, has also been

identified (Figure 9) by Energy Dispersive X-ray spectroscopy (EDX). It confirms the presence of  $\text{MnO}_2$  on the surface of coated electrode material deposited by electroplating. Table 4 depicts percentage of  $\text{MnO}_2$ , analyzed by AAS, deposited at different current density.

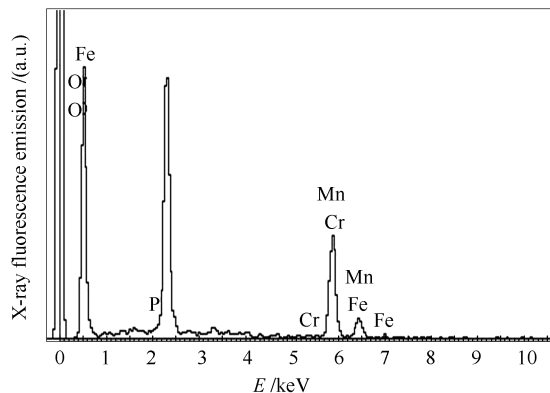


Figure 9 EDX study of  $\text{MnO}_2$  coated on 304 stainless steel at  $100 \text{ mA/cm}^2$  current density

## 2.4 SEM study for the morphology of coated deposited

$\text{MnO}_2$  performing as superior electro catalytic material for methanol fuel cell with higher delivering current and lower overvoltage are supported by SEM images morphology as shown in Figure 10. It is seen that the grain size of  $\text{MnO}_2$  is reduced with increase in current density of electrodeposition. The morphology of the deposit exhibits an effective more 3D space (Figure 10, (c), (d)) that accounts for the faster electrochemical oxidation of the fuel in the fuel cell. Some nano grains are also revealed at higher current density. Thus by controlling the current density of electro coating, a nanostructure  $\text{MnO}_2$ , energy material can be synthesized for fuel cell electrode to deliver clean energy with inexpensive materials.

Table 4 Analysis of electrodeposited alloy on by Atomic Absorption Spectrophotometer (AAS)

$\text{MnO}_2$ deposited alloy at different Cd	$\text{MnO}_2$ w/%
$50 \text{ mA/cm}^2$	10.33
$100 \text{ mA/cm}^2$	54.52
$150 \text{ mA/cm}^2$	83.89

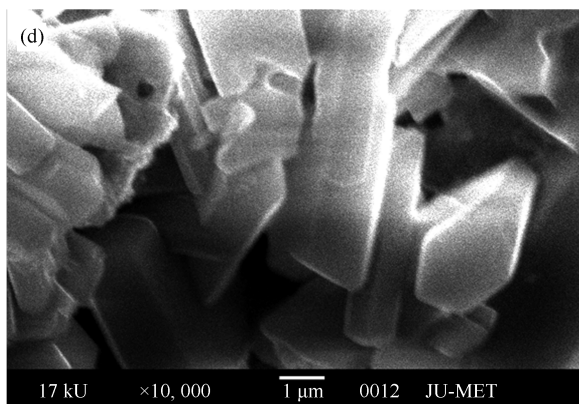
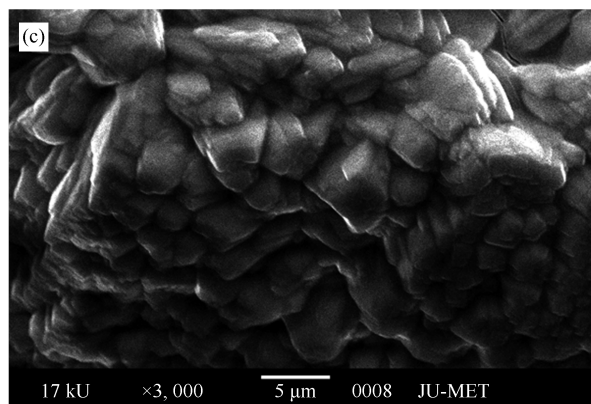
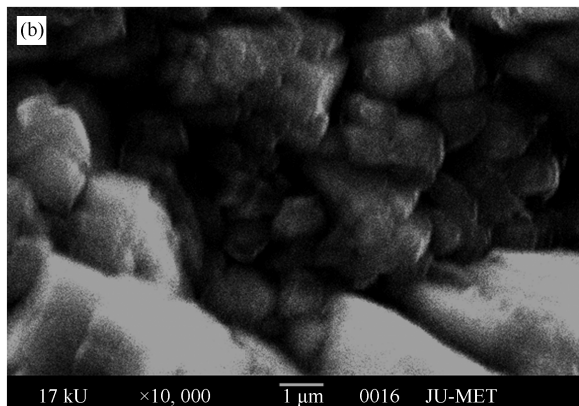
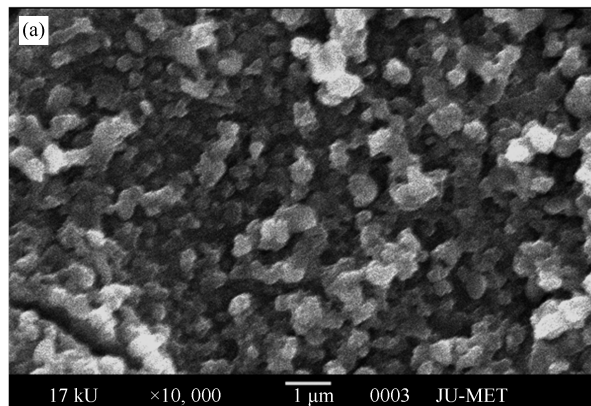


Figure 10 SEM photograph of  $\text{MnO}_2$  electrocoated samples at different current density (a) :  $50 \text{ mA/cm}^2$ ; (b) :  $150 \text{ mA/cm}^2$ ; (c) :  $100 \text{ mA/cm}^2$ ; (d) :  $100 \text{ mA/cm}^2$

## 3 Conclusions

Controlled electrodeposition parameters for

electro synthesis of  $\text{MnO}_2$  on stainless steel substrate could produce a high electrocatalytic energy materials

for fuel cell electrode, for electro oxidation of methanol at anode and H<sup>+</sup> reduction at cathode. Studies of electrochemical polarization and impedance spectroscopy showed that the material exhibits low polarization resistance and impedance; and high capacitance. This signifies that the fuel cell if fabricated with these electrodes will deliver higher

current at lower cost from an alcoholic fuel like methanol oxidation. The present investigation shows a direction of producing economically viable clean electrical energy through fuel cell, using MnO<sub>2</sub> as electrode material than conventional Pt based electrode from oxidation alcoholic fuels like methanol.

## References

- [1] PAUL S. Study on bioelectrochemical fuel cell with algae[J]. J Inst Eng (India), Environ Eng Div, 2007, **88**: 27-30.
- [2] PAUL S, MONDAL P. Pyrolysis of forest residue for production of bio fuel[J]. Int Energy J, 2006, **7**: 221-225.
- [3] PAUL S, MONDAL P. Fabrication and characterization of bioelectrochemical fuel cell with pyrolysed produced bio oil and hydrolysed biomass by fermentation[J]. J Inst Eng (India), Environ Eng Div, 2009, **90**: 40-45.
- [4] PAUL S. Characterization of bioelectrochemical fuel cell fabricated with agriculture wastes and surface modified electrode materials[J]. J Fuel Cell Sci Technol, 2012, **9**(2): 021013-18 (pages).
- [5] LEE J. Biological conversion of lignocelluloses biomass to ethanol[J]. J Biotechnol, 1997, **56**(1): 1-24.
- [6] IRANMAHBOOBA J, NADIMA F, MONEMIB S. Optimizing acid-hydrolysis: A critical step for production of ethanol from mixed wood chips[J]. Biomass Bioenergy, 2002, **22**(5): 401-404.
- [7] SCHELL D J, RILEY C J, DOWE N, FARMER J, IBSEN K N, RUTH M F, TOON S T, LUMPKIN R E. A bioethanol process development unit: Initial operating experiences and results with a corn, ber feedstock[J]. Bioresour Technol, 2004, **91**(2): 179-188.
- [8] CHAUDHURI S K, LOVLEY D R. Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells[J]. Nat Biotechnol, 2003, **21**: 1229-1232.
- [9] KIM J R, JUNG S H, REGAN J M, LOGAN B E. Electricity generation and microbial community analysis of alcohol powered microbial fuel cells[J]. Bioresour Technol, 2007, **98**(13): 2568-2577.
- [10] WANG X, FENG Y J, LEE H. Electricity production from beer brewery wastewater using single chamber microbial fuel cell[J]. Water Sci Technol, 2008, **57**(7): 1117-1121.
- [11] BASNAYAKE R, LI Z, LAKSHMI S, ZHOU W, SMOTKIN E S, CASADONTE D J, KORZENIEWSKI C. PtRu nanoparticle electrocatalyst with bulk alloy properties prepared through a sonochemical method[J]. J Am Chem Soc, 2006, **22**(25): 10446-10450.
- [12] BOCK C, PAQUET C M, COUILLARD G, BOTTON A, MACDOUGALL B R. Size-selected synthesis of PtRu nano-catalysts: Reaction and size control mechanism[J]. J Am Chem Soc, 2004, **126**(25): 8028-8037.
- [13] SHAN C, TSAI D S, HUANG Y S, JIAN S H, CHENG C L. Pt-Ir- IrO<sub>2</sub>NT thin-wall electrocatalysts derived from IrO<sub>2</sub> nanotubes and their catalytic activities in methanol oxidation[J]. Chem Mater, 2007, **19**(3): 424-431.
- [14] LUO J, NJOKI P, LIN Y, WANG L, MOTT D, ZHONG C. Activity-composition correlation of AuPt alloy nanoparticle catalysts in electrocatalytic reduction of oxygen[J]. J Electrochem Commun, 2006, **8**(4): 581-587.
- [15] CASADO-RIVERA E, VOLPE D J, ALDEN L, DOWNIE C, VAZQUEZ-ALVAREZ T, ANGELO A C D, DISALVO F J, ABRUNA H D. Electrocatalytic activity of ordered intermetallic phases for fuel cell applications[J]. J Am Chem Soc, 2004, **126**(12): 4043-4049.
- [16] CHENG S A, LIU H, LOGAN B E. Increased power generation in a continuous flow MFC with advective flow through the porous anode and reduced electrode spacing[J]. Environ Sci Technol, 2006, **40**(7): 2426-2432.
- [17] MORRIS J M, JIN S, WANG J Q, ZHU C Z, URYNOWICZ M A. Lead dioxide as an alternative catalyst to platinum in microbial fuel cells electrochem[J]. Electrochem Commun, 2007, **9**(7): 1730-1734.
- [18] LI Y, LU A H, DING H R, JIN S, YAN Y H, WANG C Q, ZEN C P, WANG X. Cr(VI) reduction at rutile-catalyzed cathode in microbial fuel cells electrochem[J]. Electrochem Commun, 2009, **11**: 1496-1499.
- [19] MOHAMEDI M, HISAMITSU Y, KIHARA K, KUDO T, ITOH T, UCHIDA I. Ni-Al alloy as alternative cathode for molten carbonate fuel cells[J]. J Alloys Compd, 2001, **315**(1/2): 224-233.
- [20] SURESH KUMAR K, HARIDOSS P, SESHADRI S K. Synthesis and characterization of electrodeposited Ni-Pd alloy electrodes for methanol oxidation[J]. Surf Coat Technol, 2008, **202**(9): 1764-1770.
- [21] PAUL S, NAIMUDDIN S K, GHOSH A. Electrochemical characterization of Ni-Co and Ni-Co-Fe for oxidation of methyl alcohol fuel with high energetic catalytic surface[J]. J Fuel Chem Technol, 2014, **42**(1): 87-95.
- [22] DAS D, SEN P K, DAS K. Electrodeposited MnO<sub>2</sub> as electrocatalyst for carbohydrate oxidation[J]. J Appl Electrochem, 2006, **36**(6): 685-690.