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Synthesis and Characterization of MnO_2 as Electrocatalytic Energy Material for Fuel Cell Electrode

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Abstract

Development Inexpensive non Pt based high electrocatalytic energy materials is the need of hour for fuel cell electrode to produce clean alternative green energy from synthesized Bio alcohol from Biomass. MnO_2 electro synthesized at different current density is found to be well performed electrocatalytic material, comparable to Pt, with higher current density, very low over voltage for electrochemical oxidation of methanol . From EIS study, the polarization resistance of the coated MnO_2 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 MnO2 deposition, the amount increases with current density. SEM morphology exhibits enhanced 3D effective substrate area for electro oxidation of the fuel and a few nano structured grains of deposited MnO2 at higher current density. The fact supports an improved electro catalytic property to be applied as high energetic materials for fuel cell Electrode.

Keywords: Electro catalytic ; Energy Material; Fuel Cell: Impedance; Polarization; Electro coating

Introduction

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 [1-4] 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_2 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 [1]. Agriculture wastes generate a huge amount of woody biomass, which can be converted to alternate fuel like bio oil [2] or to ethanol by hydrolysis and subsequent fermentation by microorganism [3-7]. 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 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 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 electrochemical oxidation of the fuel, or reduces anions at the cathode, delivering high output current from the cell. Pt having very high exchange current density for many redox systems is invariably used for laboratory scale fuel electrode. Being expensive, alternative 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 [3, 4]. 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 performance of the MFC [8]. 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 [9, 10]

Pt is an excellent catalyst for dehydrogenation but it is expensive and extremely susceptible to poisoning by CO and halides [11]. 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 [12–15]. 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 [4]. The cells produced high current of 15-25 mA/cm^2 and high power density of 10-15 mW/cm^2. The cells produced high current of 15-25 mA/cm^2 .

Non Pt 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 [16] , PbO_2 [17,], TiO_2 [18] 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) [19]. 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 [20]. Synthesis and Characterization of Ni-Co and Ni- Co-Fe on Al by electrodeposition were also investigated by us. [21]. 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 of times compared to those of bare Ni or Al surface.

There are a few works on Mno_2 based alloy electrodes development for fuel cell. Das et al developed β-MnO_2 electrocatalytic material for carbohydrate oxidation. [22].

In the present investigation attempts have been made to fabricate electrodes of $MnSO_4$+H_2SO_4 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.

Experimental Methods

304SS was used as substrate on which MnO_2 alloy was electrodeposited. The substarte was polished by 2/0 and 3/0 gradation emery paper then it is rinsed by soap water and double distilled water.

The pretreated samples were electrodeposited by the solutions of 0.34M MnSO4 salt and 0.6M of H_2SO_4 at 120°C temperature and 0.5mA/cm^2, 100mA/cm^2 150mA/cm^2 current density respectively as shown in Table I . The coated sample was rinsed by acetone and methanol one by one and then dried in an oven at 80°C overnight

For polarization study, the anodic solution was 1(M) methanol and 0.5(M) H_2SO_4, purged by argon. The cathodic solution was the mixture of 0.2(M) potassium ferricyanide and buffer (dissolve 4.08gm Na_2HPO_4 and 3.29 gm NaH_2PO_4 in 500 ml water) in 1:5 ratio purged by an air pump. Add 10ml of 0.02M of potassium hexacyano ferrate in the above solution. Electrochemical measurements were 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 MnO_2 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. A series of experiments with electrodeposited MnO_2 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_o, Corrosion potential E_{corr}, corrosion current i_{corr}, the anodic and cathodic Tafel constants β_a and β_c. The potential was scanned between -1V and 1V 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 are obtained from the EIS experiments. Polarization resistance (Rp), Electrolyte resistance (Ru),Double layer capacitance (C_{dl}), Capacitive load or Constant Phase Element ,CPE (Y), and α which is defined from the capacitive impedance equation $Z=1/C(jw)^{-\alpha}$ Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element (CPE) . The exponent α is 1 for ideal capacitance. For a constant phase element, the exponent α is less than one. The "double layer capacitor" on real cells often behaves like a CPE instead of like an ideal capacitor.

The X-ray diffraction technique is used to define the crystalline structure and the crystalline phases in each alloys 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_α radiation, at room temperature, the scan region (2θ) was ranged from 20° to 100° at a scan rate of 5° min^{-1}.

The electron micrographs were studied by SEM with accelerating voltage 30 kV, magnification up to 300,000X. 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.

Results and Discussions

Polarization of electrode surface in anodic solution (methanol solution under anaerobic condition) for the oxidation of alcohol and cathodic solution (phosphate buffer) for the reduction reaction of O_2 are given below

Anodic $CH_3OH+H_2O \longrightarrow CO_2+6H^++6e^-$, $E_a= -0.016V$ vs.SHE

Cathodic: $1.5O_2+6H^++6e^- \longrightarrow 3H_2O$ $E_c= 1.229V$ vs. SHE

H^+ generated during oxidation of alcohol gets diffused into cathodic chamber through the membrane and supply H^+ ions for cathodic reduction reaction of O_2 to pure water. In order to estimate the performance of this electrodeposited electro catalysts the following studies were performed.

Polarization studies of coated electrodes

Fig.1 displays the polarization of 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 MnO_2 produces higher current. The effect of MnO_2 alloy coating on SS at different current density in cathodic solution is also reflected in fig.2 . 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 fig3, that the MnO_2 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 (βa, βc, Ecorr, Icorr, i_o) estimated from experimental data have been illustrated in table II. It is very interesting to note that the value of i_o is increased by a few hundred times for MnO2 alloy deposition on SS, 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 elctrocatalytic properties (βa, βc, Icorr, i_o) of all the material are always better in anodic solution when methanol as fuel is electrochemically oxidized.

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 double layer, coating or film formation on surfaces, polarization resistance (R_p), Pore resistance (R_{po}) and various impedance 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.

Fig.4 shows the Bode plots for MnO2 coated electrode at different current density in anaerobic methanol solution. The curves show characteristics of Randle circuit (inset in the fig.) 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 by current density150mA/cm2) is in the range of 10-35 degree, whereas for uncoated ss surface it approaches close to 70 degree. This indicates that the interface at the electrode-solution behaves as pure capacitive load for uncoated SS and as constant phase element (which deviates from an ideal capacitor), for coated SS of higher current density. This makes charge discharge reactions faster with a coating. The Nyquist plots (fig.5) of the same experimental data show that it is a semicircle for bare SS surface with Z_{real} value quite high compared to those of coated surface,_indicating high polarization resistance of uncoated surface has been reduced a lot by alloy coating. The computed values of EIS parameter found by matching the Bode plot with an equivalent circuit close to Randle circuit with a C_{dl} parallel to R_p are illustrated table III. It is seen here that the polarization resistance R_p has been drastically reduced from 1220 ohm to order of 4.183 by alloy coating. However R_p is minimum for Pt. The constant phase element Y^0 (behaving like capacitance) increases with increase in current density of 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 hence more flow of current. This produces better electro catalytic energy material. The Y^0 value for Pt is hover highest, indicating it to be superior electro catalytic material. Similar EIS studies are shown fig 6 (Bode plots) and fig.7 (Nyquist plots). In this case also the same trend of lower impedance with higher current density of MnO2 deposition is noticed(fig6) . The phase angle vs. frequency curves are of similar nature (fig6) , but the phase angle degree for the bare surface is much more than the same for the coated surface , indicating capacitive load at the interface has been decreased by coating of MnO_2 . The EIS parameters computed from the data are illustrated in table-III. It is seen from the table that baring Pt, the coated MnO2 surface produces much lower Rp and high Y^0 with increasing current density. Y^0. Thus from the foregoing EIS results It is seen that MnO2 coated on Stainless Steel, can act as very good electrocatelytic energy material electrode in both anodic and cathodic solutions in methanol fuel cell. The degree of electro catalytic property increase when is electro synthesized at higher current density. giving 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 anions in cathodic solution at the cathode. Again **α** which signifies deviation from pure capacitive load (Table-III) also distinguishes coated and uncoated electrodes significantly. The double layer capacitance at the metal/solution interface behaves close to pure capacitance for SS and a constant phase element for coated surfaces, indicating faster charge transfer at the latter.

Y^0

XRD, EDX, AAS analysis

The X-ray diffraction of of electrocoated MnO2 (fig8a) is indicated by peaks intensity at different 2θ values. This confirms electro deposition of MnO2 on SS. The average elemental composition of different MnO2 coated on SS surface, at specific sites, during electron microscopy study, has also been identified (fig.9) by Energy Dispersive X-ray spectroscopy (EDX). It confirms the presence of MnO2 on the surface of coated electrode material deposited by eletroplating. Table-IV depicts percentage of MnO2 , analyzed by AAS, deposited at different current density,

SEM study for the morphology of coated deposited

MnO2 performing as superior electro catalytic material for methanol fuel cell with higher current delivering and lower overvoltage are supported by SEM images morphology as shown Fig.10 . It is seen grain size of MnO2 is reduced with increase in current density of electrodeposition. The morphology of the deposit exhibits an effective more 3D space (fig 10,c,d) for electrochemical oxidation of the fuel in fuel cell. Some nano grains are also revealed at higher current density. Thus by controlling current density a nanostructure MnO2 electrodeposit energy material can be synthesized for ,fuel cell.

Conclusion

Controlled Electrodeposition parameters Electrodeposition of 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^+ reduction at cathode. Studies of electrochemical polarization and impedance spectroscopy showed low polarization resistance and impedance and high capacitance. This signifies that the fuel cell fabricated with these electrodes will deliver higher current. The present investigation shows a direction of a cheaper non pt based electrode materials development for renewable energy from bio alcohols in fuel cells.

References

[1]. Paul, S., Jana, A., J. Inst. Eng. Interdisciplinary Div. 88 (2007) 27-30.
[2]. Paul, S., Mondal, P., J. Int. Energy. 7 (2006) 221-225.
[3]. Paul, S., Mondal, P., J. Inst. Eng. Interdisciplinary. 90 (2009) 40-45.
[4]. Paul, S., J. of Fuel Cell Science and Technology ASME. 9 (2012) 021013.
[5]. Lee, J., J. of Biotechnology. 56 (1997) 1– 24.
[6]. Iranmahbooba, J., Nadima, F., Monemib, S., Biomass and Bioenergy. 22 (2002) 401 – 404.
[7]. Daniel, J., Schell, et. al., Bioresource Technology. 91 (2004) 179–188.
[8[. Swades, K., Chaud, H., Lovley D. R. Nat. Biotechnol. 21 (2003) 1229–1232.
[9]. Kim, J. R., Jung, S. H., Regan, J. M., Logan B. E. Bioresour. Technol. 98 (2007) 2568–2577.
[10]. Wang, X., Feng, Y. J., Lee, H., Water Sci. Technol. 57 (2008) 1117–1121.
[11]. Basnayake, R., Li, Z., Lakshmi, S., Zhou, W., Smotkin, E. S., Casadonte, D. J., Korzeniewski, C., J. Am. Chem. Soc. 22(25) (2006) 10446-10450.
[12]. Bock, C., Paquet, C. M., Couillard, G., Botton, A., J. Am. Chem. Soc. 126 (2004) 8028-8037.
[13]. Shan, C., Tsai, D. S., Huang, Y. S., Jian, S. H., Cheng, C. L., Chem. Mater. 19 (2007) 424-431.
[14]. Luo, J., Njoki, P., Lin, Y., Wang, L., Mott, D., Zhong, C., J. Electrochem. Commun. 8 (2006) 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., J. Am. Chem. Soc 126 (2004) 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” Environ. Sci. Technol. 2006, 40: 364–369.
[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. Commun. 2007 9:1730–1734.
[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. Commun. 2009,11: 1496–1499.
[19]. Mohamedi M, Hisamitsu Y, Kihara K, Kudo T, Itoh T, Isamu Uchida, “Ni–Al alloy as alternative cathode

for molten carbonate fuel cells ,"Original Research Article Journal of Alloys and Compounds, 2001, 315: 224-233.

[20]. Suresh Kumar K., Haridoss Prathap, Seshadri S.K., " Synthesis and characterization of electrodeposited Ni–Pd alloy electrodes for methanol oxidation," Original Research Article. Surface and Coatings Technology,2008, 202 : 1764-1770.

[21]. Paul, S., Sk Naimuddin, Sk., Ghosh, A., J. Fuel Chem. & Tech. 42(01) (2014) 87-95

[22]. DAS D., SEN P. K. and DAS K., "Electrodeposited MnO2 as electrocatalyst for carbohydrate oxidation", Journal of Applied Electrochemistry, 2006, 36: 685–690

Table I

Controlling parameters Electro coating MnO_2

Substrate	**Electrolyte Chemistry**	**Current density mA/cm2**	**Time min**	**Temp °C**
304 steel	0.6M MnSO4 + 0.34M H2SO4	50	45	120
		100	‘’	‘’
		150	‘’	‘’

Table II

Comparison studies of experimental computed electrcochemical kinectic data of different coated metals and bare metal, in anodic solution (anaerobic methanol solution) and , in cathodic solution (phosphate buffer solution)

Material	**In anodic solution (anearboic methanol solution):**					**In cathodic solution (phosphate buffer solution)**				
MnO_2 coated at cd	**β_a mv**	**β_c mv**	**Icorr µA/cm²**	**Ecorr V**	**Io µA/Cm^2**	**Ba mv**	**β_c mv**	**Icorr µA/cm²**	**Ecorr V**	**Io µA/Cm²**
50mA/cm2	115	133.4	98.8	0.238	2.17	289.6	168	91.8	-0.488	1.83
100mA/cm2	196.7	198.2	58.3	0.120	20.4	372.5	176.8	65.8	-0.507	2.01
150mA/cm2	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	.395	1.88	94.01	37.8	921	-0.378	1.72

Table III

Comparison studies of experimental computed Electrochemical Impedance Spectroscopy data of different coated samples and bare metal, in anodic solution (anaerobic methanol solution) and, in cathodic solution (phosphate buffer solution)

	anodic solution (anearboic methanol solution)				**cathodic solution (phosphate buffer solution)**			
50mA/cm2	299.1	4.802	61.87	0.272	913.3	18.96	645.9e-3	0.179
MnO_2 coated at cd	**Rp Ohms**	**Rs Ohms**	**Y^o(S*s^a) µF**	**α**	**Rp Ohms**	**Rs Ohms**	**Y^o(S*s^a) µF**	**α**
100mA/cm2	81.21	4.183	66.89	0.249	634.9	38.04	700.6e-3	0.187
150mA/cm2	31.36	2.462	82.46	0.179	156.3	42.34	767.4e-3	0.176
Pt sample	26.63	3.703	109.83	0.125	126.5	75.47	788.8e-3	0.103
Bare 304 SS	891	1220	4.222	0.388	1.349e3	18.57	496.5e-3	0.339

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

MnO2 Deposited alloy at different Cd	**% of MnO2**
50mA/cm2	10.33
100mA/cm2	54.52
150mA/cm2	83.89

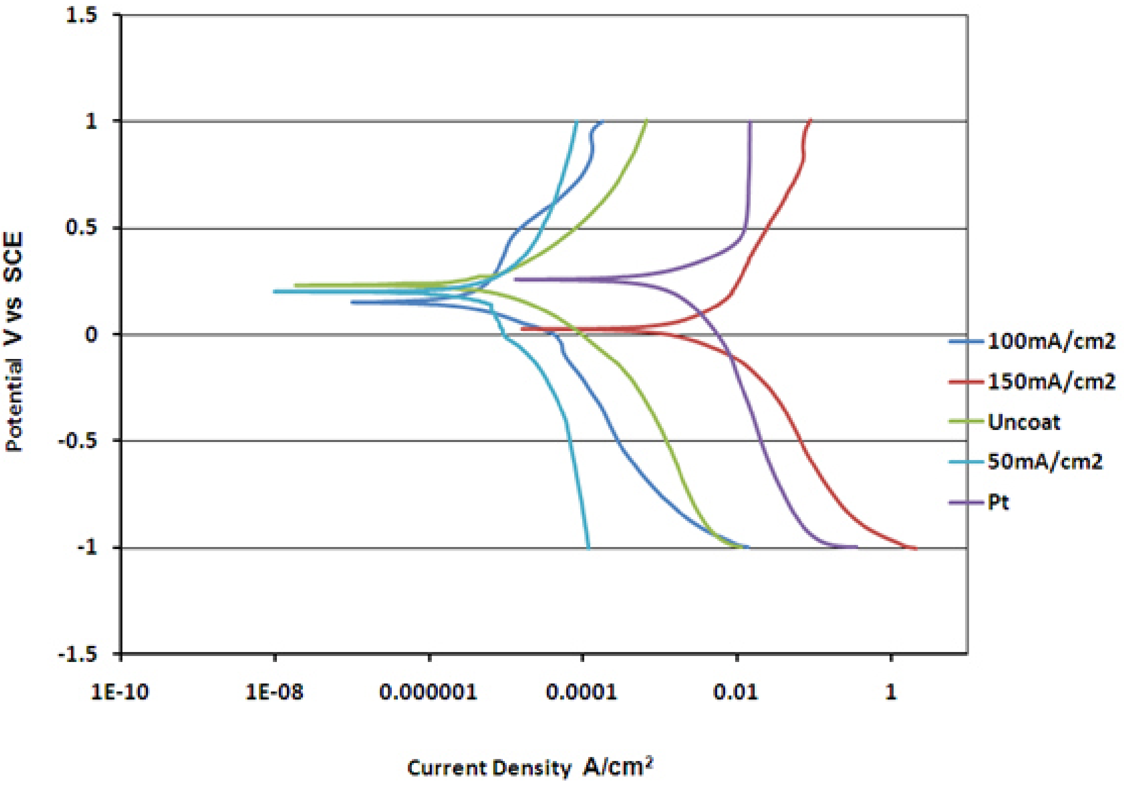


Fig 1: Polarization of Curves of electro coated MnO_2 at different Current density, in methanol solution under anaerobic condition at 25°C (anodic solution) , the same for 304 steel and Pt are given for comparison

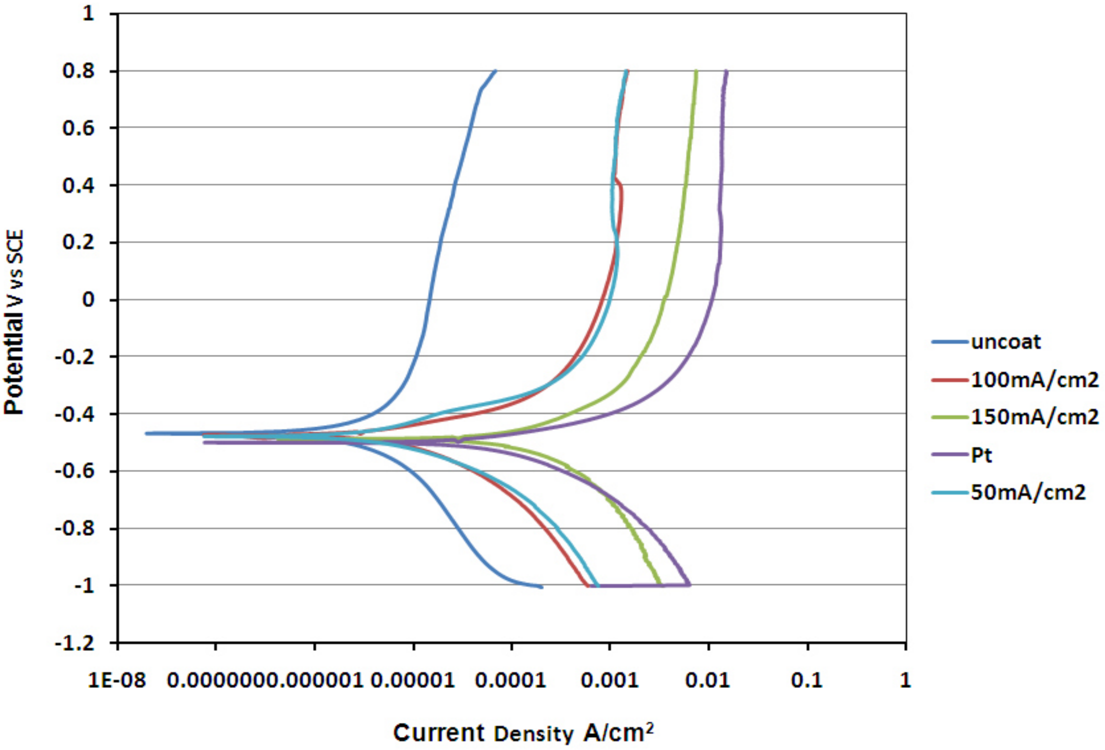
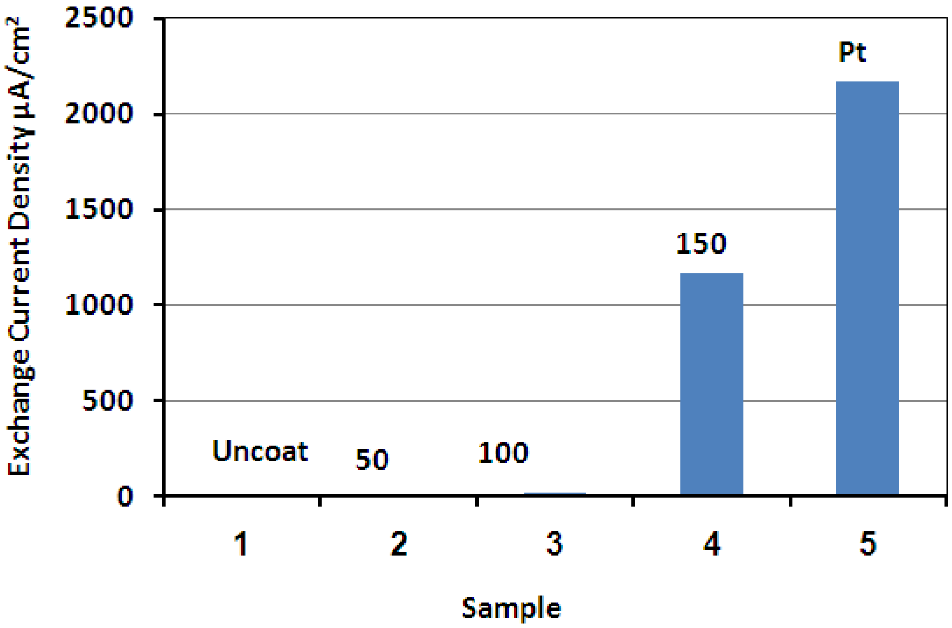
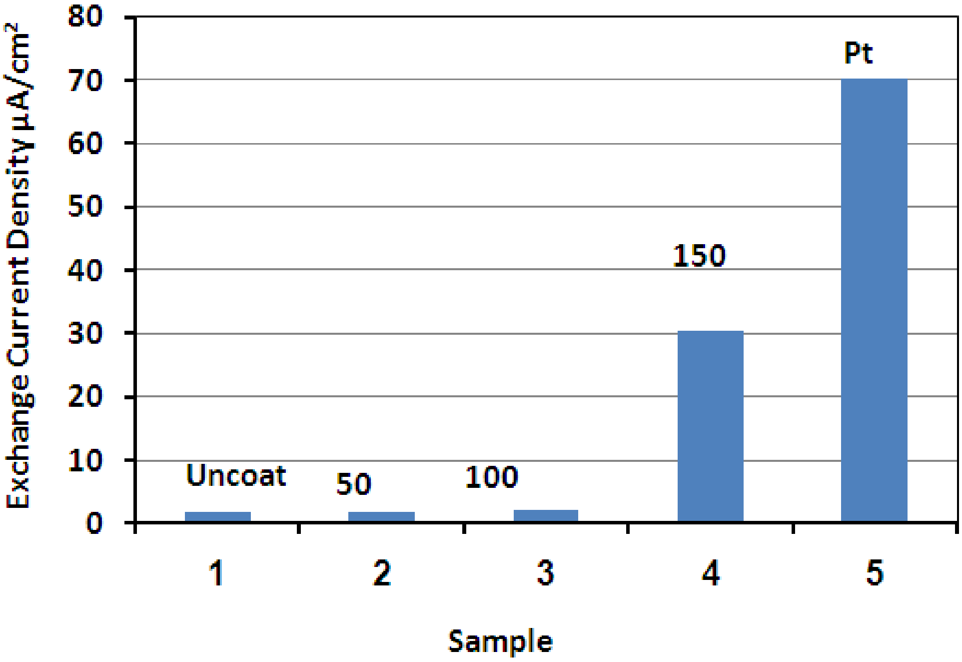


Fig 2: Polarization of Curves of electro coated MnO_2 at different Current density in aerated phosphate buffer solution at 25°C (Cathodic Solution), the same for 304 steel and Pt are given for comparison



i) anodic solution (anaerobic methanol solution)



ii)cathodic solution (aerated phosphate buffer solution)

Fig 3:Comparison of exchange current density of electro coated MnO_2 at different Current density, the same for 304 steel and Pt

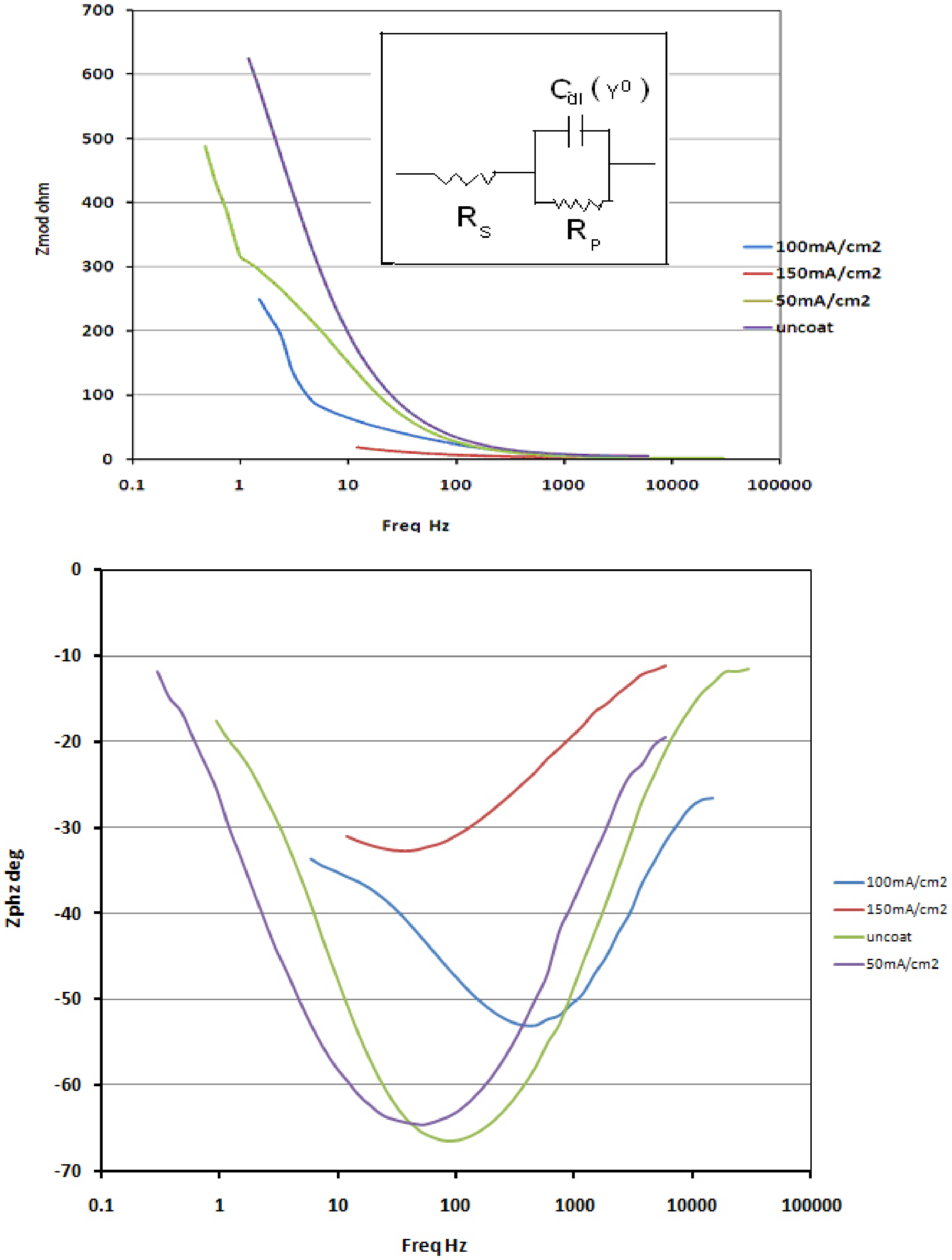


Fig 4: Bode plot electro coated MnO_2 at different Current density, in methanol solution under anaerobic condition at 25°C (anodic solution) , the same for 304 steel and Pt are given for comparison

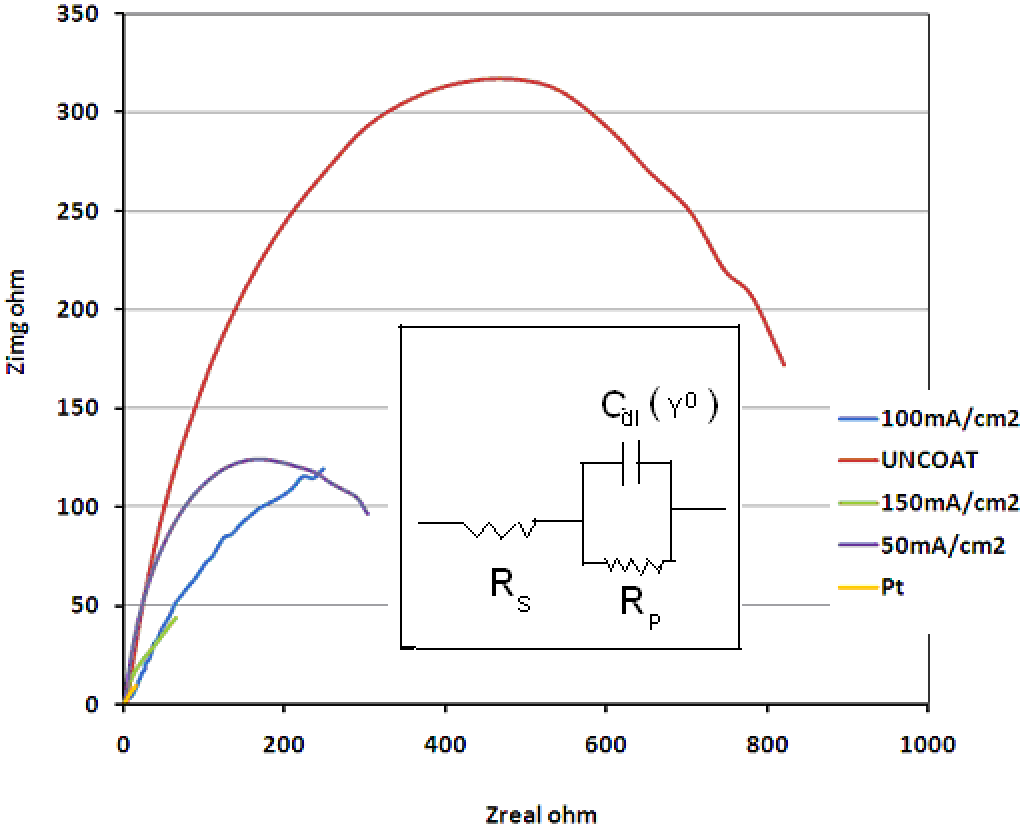


Fig 5: Nyquist plot electro coated MnO_2 at different Current density, in methanol solution under anaerobic condition at 25°C (anodic solution) , the same for 304 steel and Pt are given for comparison

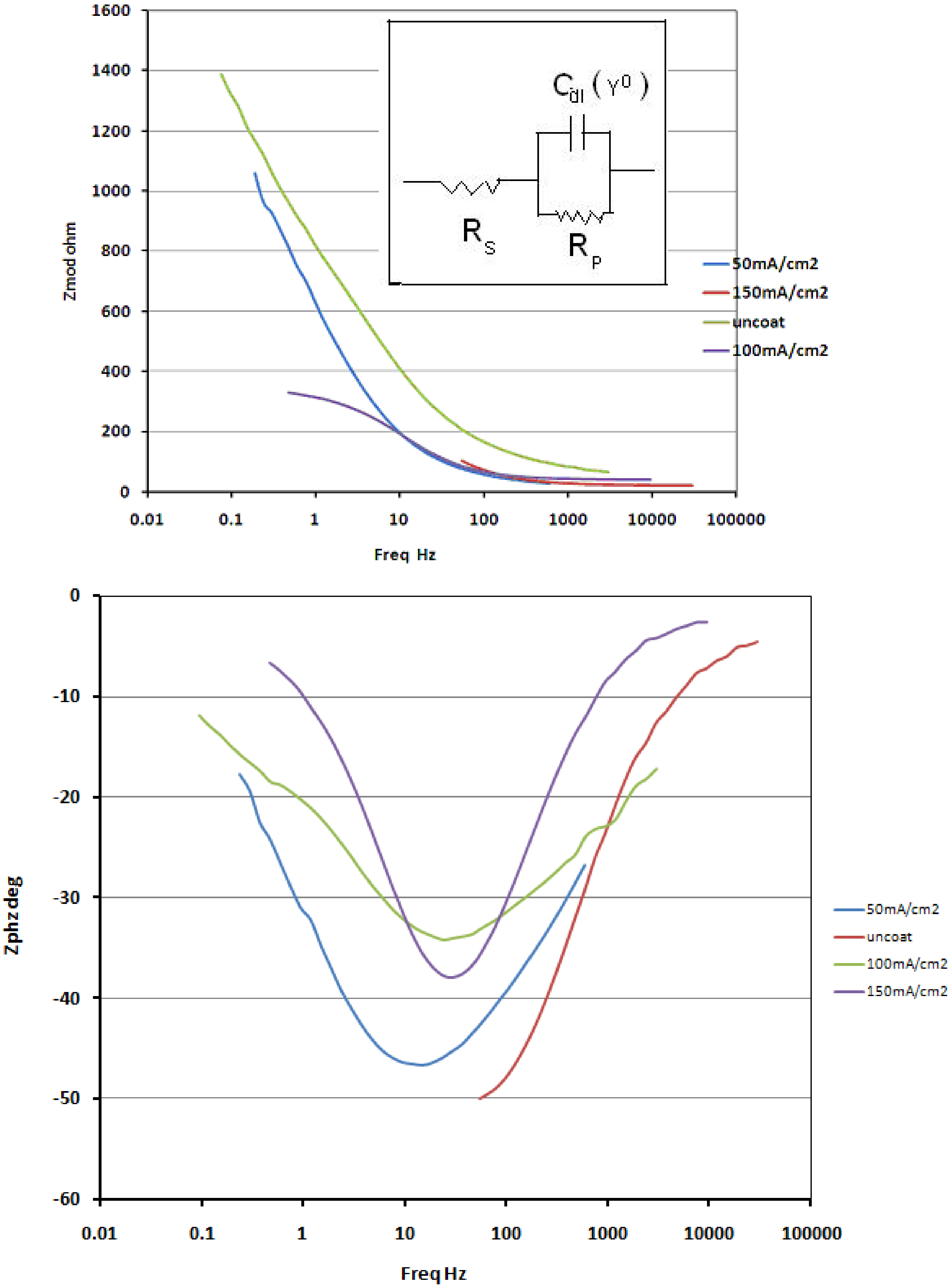


Fig 6:Bode plot of electro coated MnO_2 at different Current density in aerated phosphate buffer solution at 25°C (Cathodic Solution), the same for 304 steel and Pt are given for comparison

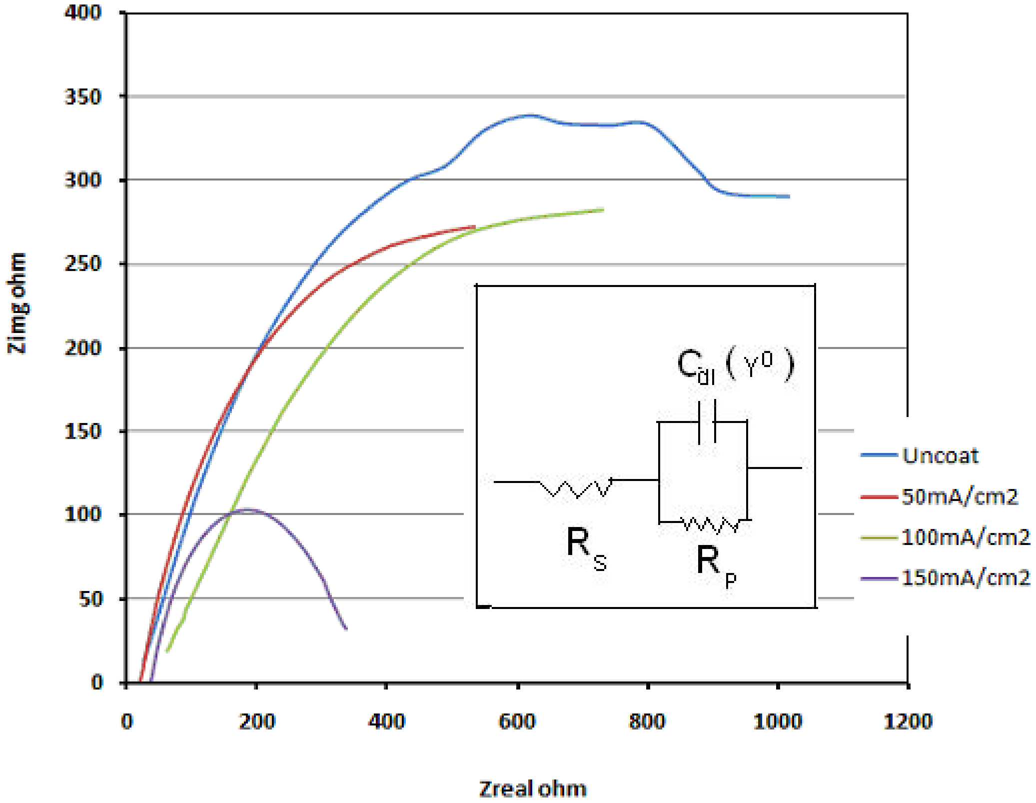


Fig 7:Nyquist plot of electro coated MnO_2 at different Current density in aerated phosphate buffer solution at 25°C (Cathodic Solution), the same for 304 steel and Pt are given for comparison

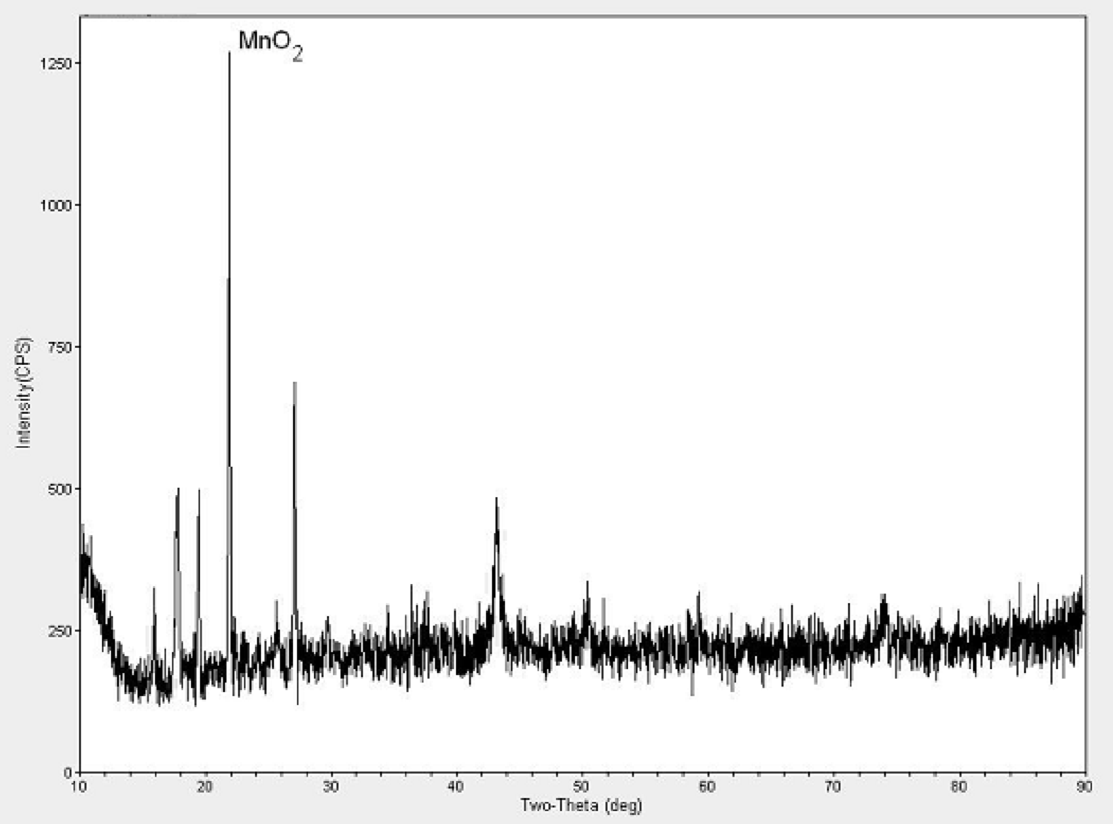


Fig 8. XRD of coated MnO_2 sample at 100mA/cm2 current density

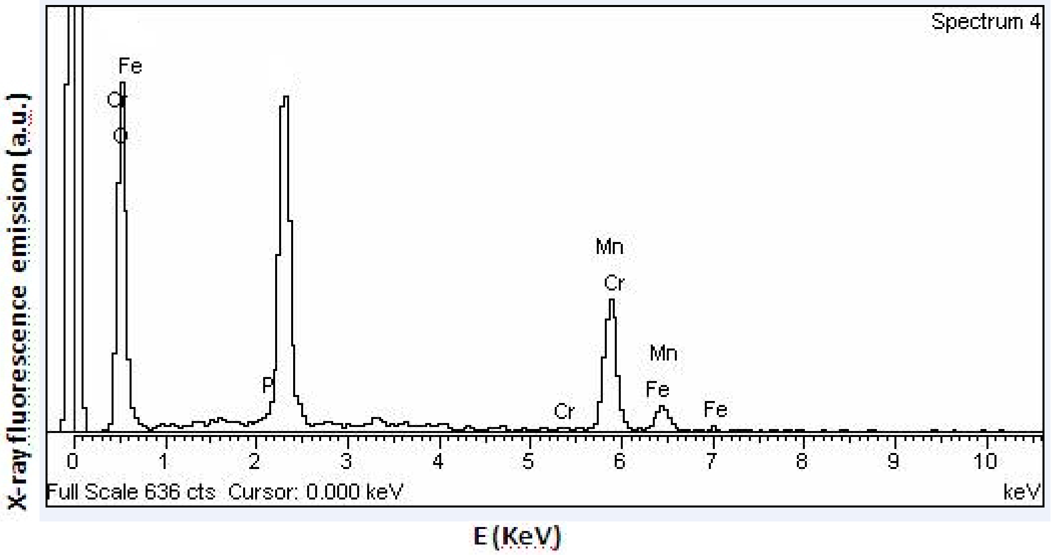
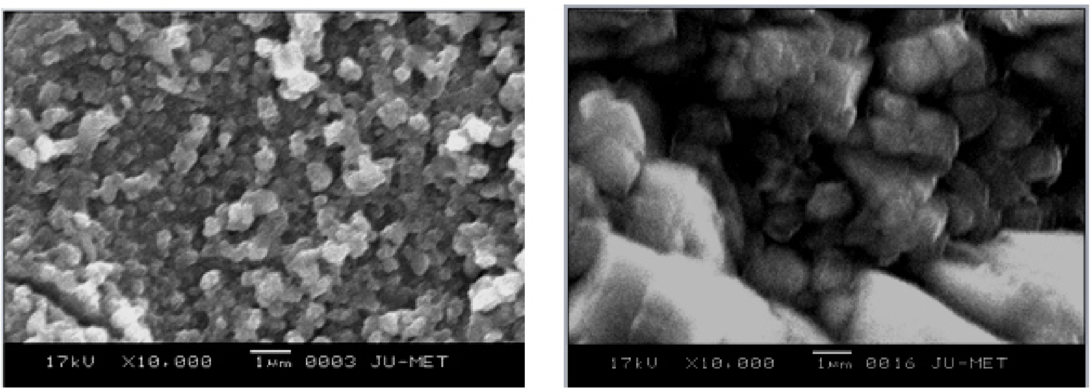
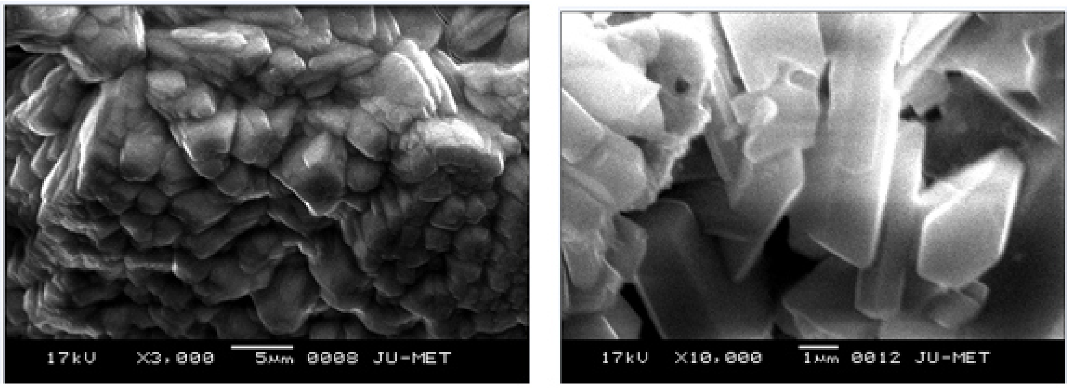


Fig 9. EDX study of MnO_2 coated on 304 stainless steel at 100mA/cm2 current density



a. 50mA/cm2

b. 150mA/cm2



c. 100mA/cm2

d. 100mA/cm2

Fig 10. SEM photograph of MnO_2 electrocoated samples at different Current density

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