

Studying the Corrosion Behavior of Nanograde Pt–Ru/C Catalyst Used In Direct Ethanol Proton Exchange Membrane Fuel Cells (DEPEMFC)

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Abstract

The corrosion behaviour of nano grade Pt–Ru (40%:20% by wt.)/C catalyst used in Direct Ethanol Proton Exchange Fuel Cells (DEPEMFC) at a loading of 1 mg/cm² was studied in different ethanol concentrations e.g., 1M and 5M by varying the speed of agitation (250, 750 and 1500 RPM) at a temp. of 80°C . The results reveal that variation in speed of agitation and ethanol concentrations plays an important role in corrosion rate. The corrosion rate is increased with increasing the concentration of ethanol from 1M to 5M at different RPM e.g., 250, 750 and 1500 RPM. The results also showed the possibility of the initiation of pitting corrosion on the Pt, Ru and C catalyst surface due to the effect of galvanic coupling generated among these metals .

Keywords : Corrosion, Pt–Ru/C Electrode Catalyst ,Direct Ethanol Proton Exchange Membrane Fuel Cell (DEPEMFC), Potentiodynamic Polarization.

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Introduction

Direct Ethanol Proton Exchange Membrane Fuel Cells (DEPEMFC) deliver high power density, which offers low weight, cost and volume. It operates at low temperature (i.e. 80 °C), allowing for faster startups and immediate response to changes in the demand for power 'Alkire[1]'.

Ethanol can be produced in large quantities by fermentation of sugar containing bio mass resources and is thus renewable in nature .The energy density of ethanol (8030 Wh kg⁻¹) and Ethanol is less toxic than other fuels such as Methanol .Therefore efforts to use of the so-called bio-ethanol for operating PEMFC to be installed as a power source to run mobile phones, portable PCs, vehicle engines are obvious in considerable manner ' Basu[2], Fujiwara[3], Basu[4]' .On the other hand, bio-ethanol used for the above mentioned operations contains water molecules which was found surprisingly aggressive toward metallic materials and more detailed electrochemical kinetics of metal electrode in this medium are yet unknown ' Souza[5] '.

Therefore understanding the root causes for the corrosion failures in DEPEMFC is an ultimate goal of this investigation because electrochemical reactions occur within the electrode assembly such as the anodic reaction, and thus, the latter is a key component of a fuel cell. In other words the above mentioned understandings will be reflected directly on reducing the direct and indirect economic losses (i.e. replacement of corroded parts, shut down of DEPEM Fuel Cell), because the durability of DEPEMFC is affected by both its physical properties and the fuel cell operating conditions. The state of the art fuel cell electrode is normally composed of carbon-supported noble metal catalyst such as Pt-Ru. The carbon support provides several desired functions. First, it enables the uniform dispersion of Pt/Ru particles. Second, it retards the sintering or agglomeration of Pt/Ru particles. Third, it provides electronic continuity. Carbon as a support has good chemical and electrochemical stabilities, and these properties make it popular fuel cell catalyst support. The aim of the present investigation is to study the corrosion behavior of Pt-Ru/C with at a loading of 1 mg/cm² used as catalyst on a treated carbon sheet covered with a layer of carbon black to be kept inside a special holder made of Perspex material with an opening of 4 cm² to expose the Pt,Ru/C layer to the corrosive environment. Different ethanol concentrations were used during the investigation e.g., 1M and 5M and different RPM e.g., 250, 750 and 1500 RPM. at a temp. of 80°C. The potentiostat was used to accelerate the corrosion reaction by applying potential across the working electrode and the counter electrode, then to measure the half cell potential using Ag/AgCl reference electrode in order to draw the potentiodynamic polarization curve and as result conducting

Tafel extrapolation to calculate the corrosion rate at each operating condition in order to simulate the actual corrosion behavior of the anodic portion used in DEPEMFC according to the following oxidation reaction :



Experimental

Materials :

The catalyst used to prepare the electrode was Nano grade Pt-Ru (40% : 20% by wt.)/C from Johnson Matthey Inc.,UK . Carbon black , Vulcan XC 72 R, GP-3915 obtained from CABOT Co. which was used as a primary substrate layer. Carbon paper (Lydall 484C-1,USA) used as a substrate for the catalyst powder . A mixture of Nafion[®] (SE-5112,Dupont USA) and 1-Propanol (MERK) was used as a binder. Ethanol (MERK) and distilled water was used as an electrolyte.

Preparation of the working electrode

The working electrode was prepared by cutting a 3 x 3 cm. from the Carbon sheet. Preparing a slurry of Carbon black powder dispersed in 1-Propanol using an ultrasonic water bath for 30 min. . The Carbon Black slurry was uniformly spread on an area of 2 x 2 cm. in the middle of the above mentioned 3 x 3 cm. Carbon sheet. It was then dried in an oven for 1 hr. at 100 °C. The weight of dried electrode was measured using a digital balance and kept in a special plastic bag .

Weighing 4 mg of the Nanograde Pt-Ru (40% : 20% by wt.)/C powder using a digital balance and then dispersing the required quantity of the catalyst powder in 4 drops of Nafion solutions and 5 drops of 1-propanol then keeping the mixture in an ultrasonic water bath for 30 min. The catalyst slurry was uniformly spread in the form of continuous wet film using a brush over the above mentioned 2 x 2 cm. Carbon Black layer on the surface of the carbon sheet . Then the working electrode was dried in an oven for 1hr. at 100 °C. . The weight of the dried electrode was measured using a digital balance to ensure that 4 mg. of the catalyst spread on the surface of the electrode and kept in a special plastic bag to keep it dry .

Experimental setup and method

Electrode holder setup

A circular shaped working electrode holder setup was designed and fabricated from Perspex sheet to hold the working electrode in a square having a slot of 0.1 mm in depth and 3×3 cm. in area and then to be covered from the top with circular shaped cover made of Perspex having an opening of 2×2 cm. in order to keep an area of 4 cm^2 of the working electrode to be exposed to the corrosive environment. Plastic bolts and nuts were designed and fabricated in order to attach tightly the cover to the working electrode holder. A special tunnel was drilled in the circular electrode holder in order to enable the insertion of an electric wire used as a conductive path between the bottom of the working electrode surface and the potentiostat keeping in mind that the bottom surface is not exposed to the mentioned corrosive environment. Teflon tape was used to prevent leakage of the electrolyte to the undesired parts of the working electrode. Figs.(1–2), show the above mentioned circular shaped electrode holder setup.

Methodology

Before starting the experiment, the desired electrolyte was kept in 2 lit. glass beaker then to be inserted into the water bath in order to increase the temp. of the electrolyte to 80°C . Then the Perspex electrode holder setup was inserted inside the electrolyte at the desired temp. and connected to the potentiostat. Platinum electrode was used as a counter electrode while Ag/AgCl was used as a reference electrode and all were connected to the potentiostat. A glass stirrer connected to an automatic agitator was used to vary the speed of agitation as shown in fig.(3). The potentiostat was kept on the run mode by clicking the start button in the operating software package in order to draw the potentiodynamic polarization curve at scan rate of 0.05 V/Sec. with step potential of 25 mV for 1 hr. The corrosion rate was calculated at the end of the each experimental run using the same software package to conduct Tafel extrapolation at each operating condition. Each condition was repeated for two times and in some cases for three times in order to check the degree of reproducibility among the results. Before conducting the experiments, the free corrosion potential of the working electrode was also measured using the voltmeter and the reference electrode.

Results and discussion

Effect of Ethanol concentration and speed of agitation on corrosion rate of Pt–Ru/C catalyst layer

It is obvious from the corrosion rates given in tables (1–2) and figs.(4–6), that the corrosion rate is increased with increasing the concentration of ethanol from 1M to 5M at different RPM e.g., 250, 750 and 1500 RPM .This behaviour indicates that the electrochemical reaction is under the effect of concentration polarization following equ.(2) ' Fontana [6], Uhlig [7], Revie [8], Bard [9], Kane [10] ' :

$$\eta = \pm \beta \log (1 - i/i_L) \quad (2)$$

Where η = overpotential, β = Tafel constant = $2.3 RT / \alpha n F$. On the other hand i_L is the limiting diffusion current = $nFkC_b$, k = mass transfer coefficient and C_b is the bulk concentration .

Effect of Galvanic Coupling

The galvanic coupling among dissimilar metals can be treated by application of Mixed Potential theory ' Fontana [6], Uhlig [7], Revie [8], Bard [9], Saeed [11] '.Therefore , in the case of Pt–Ru (40% : 20% by wt.)/C three metals are connected to each other forming a galvanic active combination ' Saeed [11], David [12], West [13],Lee[14] '.The response of this combination to the corrosive environment differs from the behavior of these metals when they are not connected to each other , because each metal has its own exchange current density (i_o) and Equilibrium Potential (E_{eq}) and as a result the corrosion current ($i_{corr.}$) will deviate in its position towards the coupling potential ($E_{coupling}$) rather than the corrosion potential of the metal when it is alone. It is obvious that $E_{coupling}$ at any time represents the result of the galvanic interaction and electromotive force between different metals. Furthermore ,the summation of galvanic currents on the three metals is equal to zero , $\sum I_g = I_g Pt + I_g Ru + I_g C = 0.0$ (i.e. $\sum I_a = \sum I_c$) ' Saeed [11], West [13] '.

As a result of this assumption the metals in the combination might show an increase in the current to less negative values and other might show a decrease in the current to less positive values. In other words, the behaviour of these metals in the given environment might respond in different manners so the more negative (active) metal in the combination might corrode sacrificially and get depleted to protect the other metals of less negativity (i.e. More Noble). This act is also affected with the surface area of each metal in the couple as an important variable. In our case Ru % is less than Pt% and C % and as a result there will be a difference in the area ratio of cathodic elements in the combination to anodic elements in same combination (i.e. A_c/A_a) raising the act of the sacrificial depletion of the most active metal in the combination to protect the other elements (i.e. more noble) by generating a very small (i.e tiny currents) negative and positive so that the summation of the galvanic anodic currents generated by the three metals (i.e. $\sum I_{g,a}$) will be gathered by the most active metal in the combination while the summation of the galvanic cathodic currents (i.e. $\sum I_{g,c}$) will be gathered by the most noble metals in the combination' Saeed [11], West [13], Lee [14] '. As a result galvanic corrosion will occur which will encourage the formation of pitting corrosion. The stereomicroscopic analysis for the surface of selected samples as shown in figs(7 and 8) in which the red circles refer to the severely corroded areas due to pitting corrosion as a result of galvanic corrosion .

Conclusions

Studying the corrosion behavior of Pt–Ru (40%:20% by wt.)/C catalyst layer which is used in DEPEMFC in two different ethanol concentrations and various speed of agitation at 80 °C showed that the electrochemical oxidation reaction of Ethanol given in equ.(1) :



On Pt–Ru (40%:20% by wt.)/C catalyst layer is under the control of concentration polarization because the corrosion rate is increased with increasing the concentration of ethanol from 1M to 5M at different RPM e.g., 250, 750 and 1500 RPM .

On the other hand ,Pt–Ru (40% : 20% by wt.)/C catalyst layer represents the case of three metals in connection to each other forming a galvanic active combination. Therefore the possibility of the initiation of pitting corrosion on the Pt, Ru and C catalyst surface due to the effect of galvanic coupling was obvious from the results .

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Table (1) : Corrosion rate of Pt-Ru/C catalyst in 1 M Ethanol

Speed of agitation ,RPM	Corrosion Rate , $\mu\text{m/y}$
250	21.8
750	17.48
1500	31.7

Table (2) : Corrosion rate of Pt-Ru/C catalyst in 5 M Ethanol

Speed of agitation ,RPM	Corrosion Rate , $\mu\text{m/y}$
250	27
750	51
1500	36

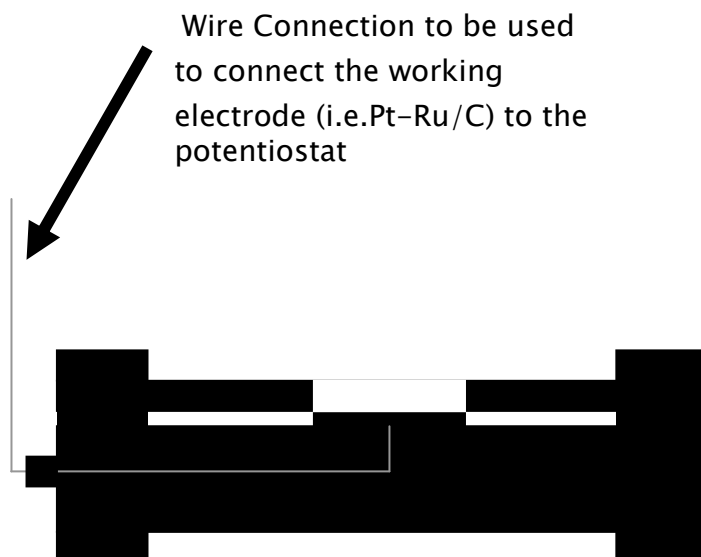


Fig.(1) Front view of the Perspex electrode holder setup with bolts and nuts made of Plastic material used to tighten the two circular parts of the electrode holder.

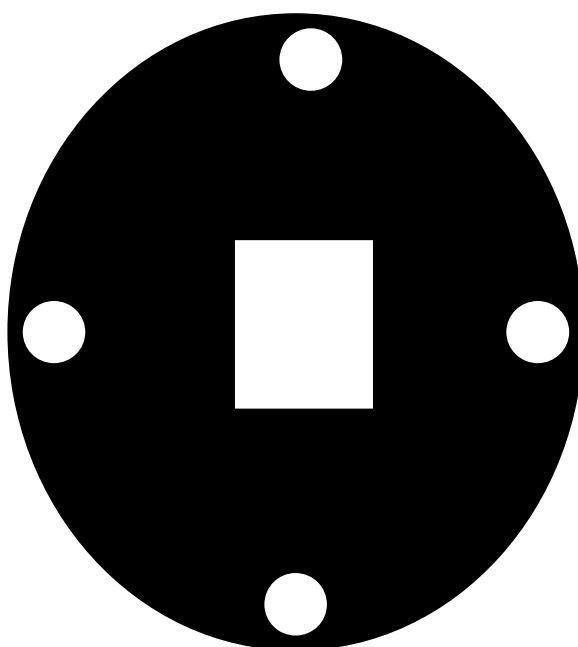


Fig.(2) Top view of the Perspex electrode holder setup with bolts and nuts made of Plastic material used to tighten the two circular parts of the electrode holder.

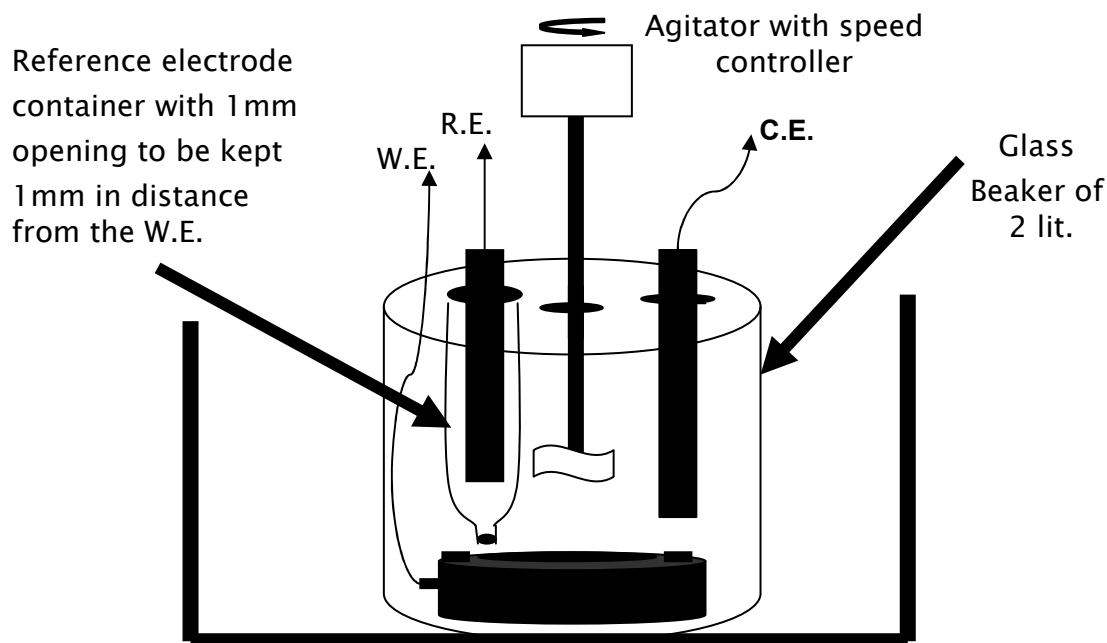


Fig.(3) Sketch of the experimental corrosion cell setup

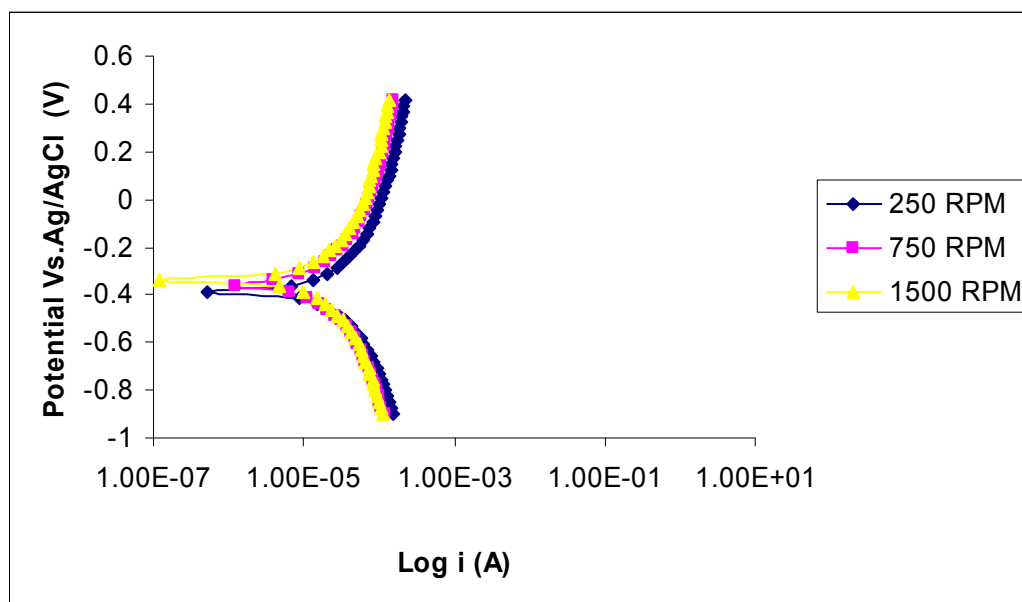


Fig.(4) Potentiodynamic polarization curves of Pt-Ru (40% : 20% by wt.)/C in 1 M ethanol, for 1 hour at 80 °C , different RPM e.g., 250, 750 and 1500

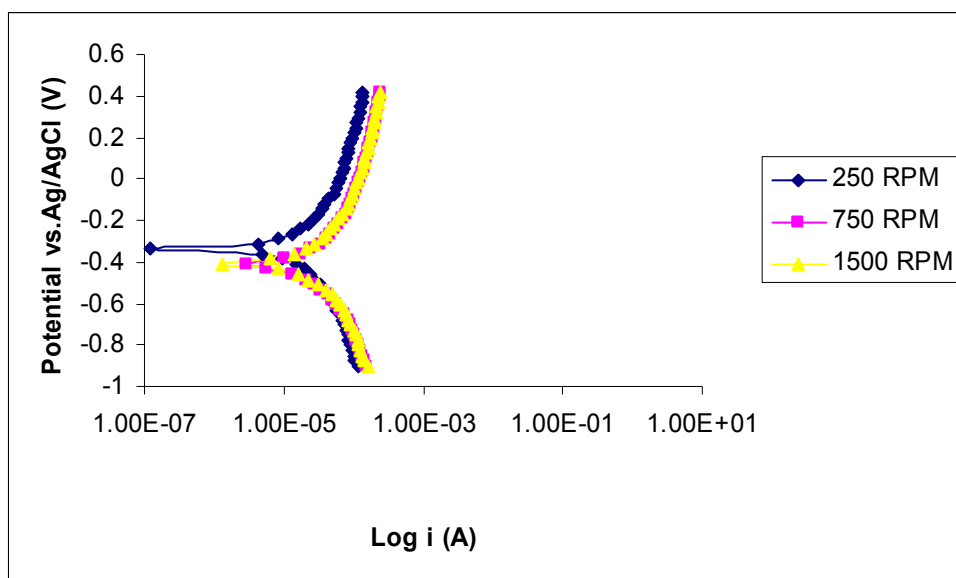


Fig.(5) Potentiodynamic polarization curves of Pt-Ru (40% : 20% by wt.)/C in 5 M ethanol, for 1 hour at 80 °C , different RPM e.g., 250, 750 and 1500 .

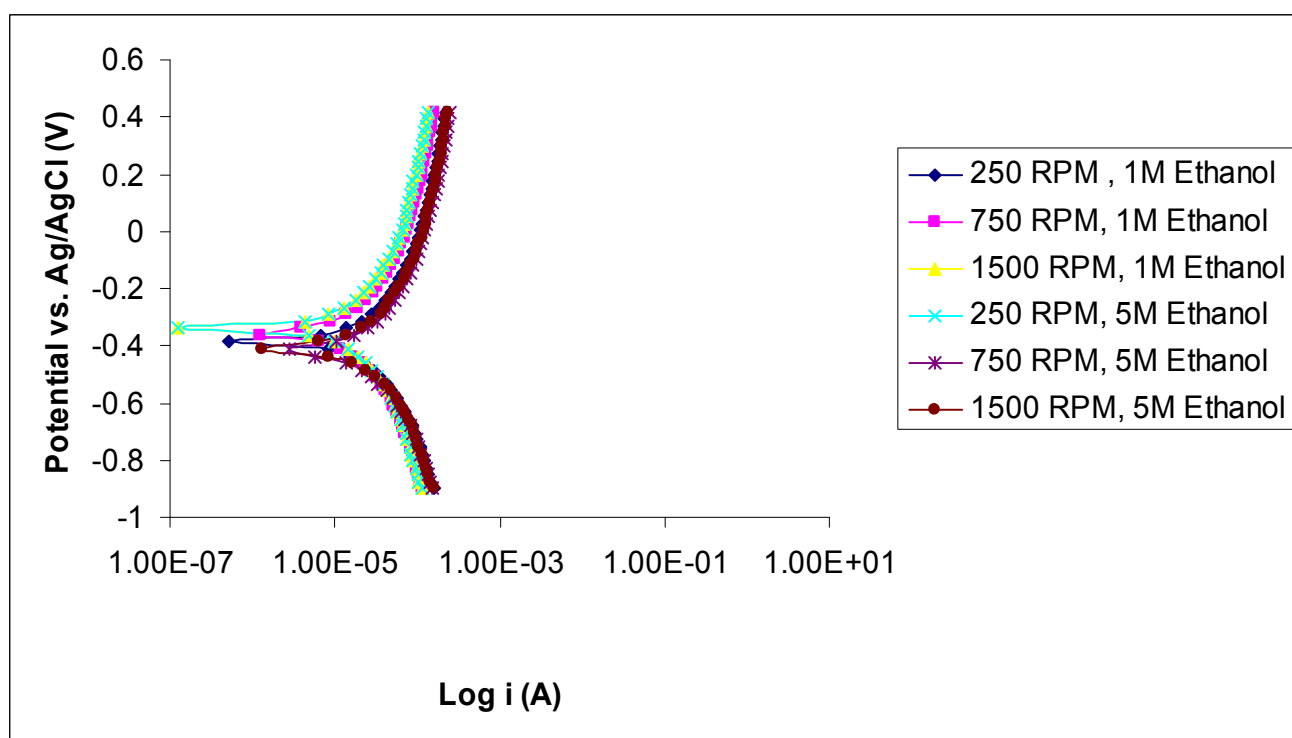
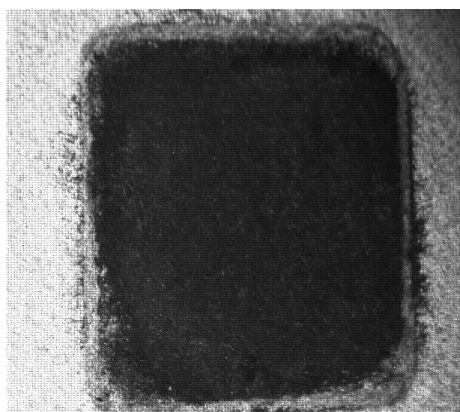
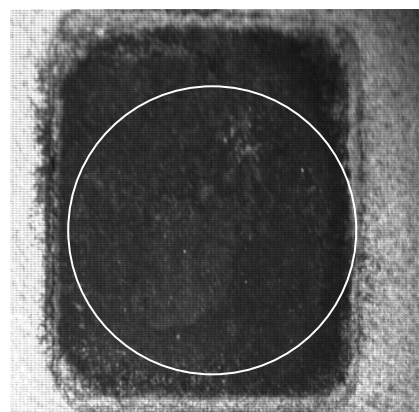


Fig.(6) Potentiodynamic polarization curves of Pt-Ru (40% : 20% by wt.)/C in 1 M and 5M ethanol, for 1 hour at 80 °C , different RPM e.g., 250, 750 and 1500 .

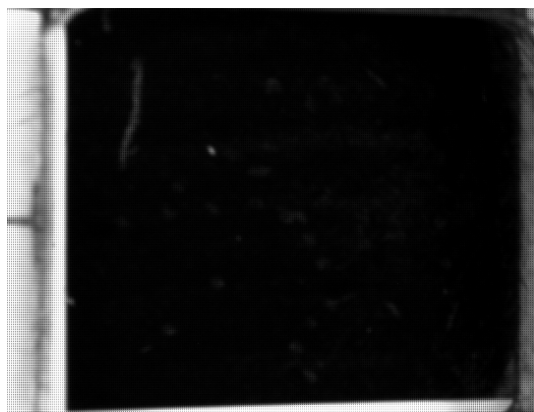


(a)

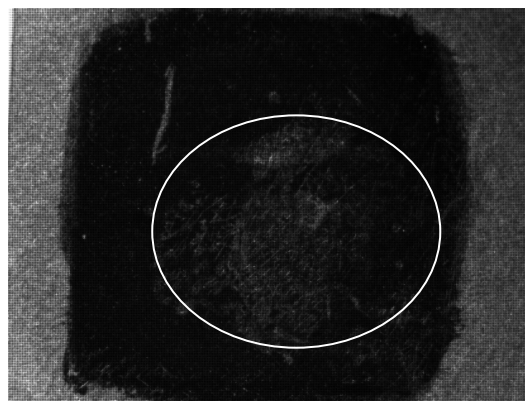


(b)

Fig.(7) (a) Pt-Ru /C layer before exposure to the corrosive environment (b) Pt-Ru /C layer after exposure to the corrosive environment 1 M Ethanol after 1 hour at 80 °C , speed of agitation equal to 250 RPM .The white circle in the stereomicroscopic image (b) without magnification show clearly the degree of depletion of Pt-Ru /C layer by forming a group of pits due to galvanic corrosion.



(a)



(b)

Fig.(8) (a) Pt-Ru /C layer before exposure to the corrosive environment (b) Pt-Ru /C layer after exposure to the corrosive environment 1 M Ethanol after 1 hour at 80 °C , speed of agitation equal to 1500 RPM . The white circle in the stereomicroscopic image (b) without magnification show clearly the degree of depletion of Pt-Ru /C layer by forming a group of pits due to galvanic corrosion.

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