Corrosion Behavior of Pt-Ru/C Catalyst Used in Direct Ethanol Fuel Cell

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Abstract

The corrosion behavior of Pt-Ru (40%: 20% by wt.)/C catalyst used in direct ethanol fuel cell at a loading of 1 mg/cm^2 was studied in different ethanol concentrations e.g., 1 M and 5 M by varying the agitator speed e.g., 250, 750 and 1500 RPM at 80° C close to working electrode. The results revealed that the variation in speed of agitation and ethanol concentrations plays an important role in corrosion rate. The corrosion rate increased with the increase in concentration of ethanol from 1 M to 5 M and agitator speed from 250 to 1500 RPM. The photomicrograph of Pt-Ru/C catalyst layer on carbon paper before and after exposure to 1 M ethanol and 0.5 M H_2SO_4 at 80 ^{o}C clearly shows the presence of corrosion mark and eventual loss of catalyst material from the carbon paper. The results reveal the possibility of initiating galvanic corrosion due to the presence of combination of Pt, Ru and C in the catalyst layer of direct ethanol fuel cell.

Keywords: Corrosion, Pt-Ru/C Catalyst, Direct Ethanol Fuel Cell

Introduction

Direct alcohol fuel cell (DAFC) is developed by many investigators for portable application. The use of ethanol as fuel in DAFC is more justified than methanol due to ethanol's intrinsic advantages such as its non-toxicity, less volatility than methanol and renewability with high energy density (8.0 kWh/kg) [1]. Furthermore its easy production in great quantities by fermentation from sugar containing agricultural wastes adds up to its advantages. The molecular size of ethanol is larger than methanol and thus helps in limiting the crossover through membrane from anode side to cathode. Therefore efforts have been to operate direct ethanol fuel cell (DEFC) as a power source to run mobile phones, laptops, digital cameras. However, DEFC delivers relatively less power density compared to direct methanol fuel cell (DMFC) because of difficulty in complete electro-oxidation of ethanol and breaking C-C bond at low temperature [2, 3, 4]. Bio-ethanol used in DEFC contains water molecules which was found surprisingly active toward metals used as electro-catalyst in DEFC. The details of

ethanol corrosion on mild steel (AISI 1005) with and without corrosion inhibitor ethanolamines is studied extensively by De Souza et al. [5]. Their investigation mainly restricted to corrosion measurement though impedance techniques.

Understanding the root cause for the corrosion failure in DEFC is the goal of this investigation because electrochemical reactions occur at the electrode plays crucial role in generating electricity during DEFC operation. The oxidation reaction occur at the anode electrode of DEFC is shown below.

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \qquad (1)$$
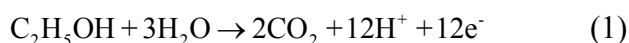
The study will be useful in determining the durability of DEFC as the corrosion will affect the electrode's physical properties and electrochemical reaction of the fuel cell. DEFC anode-electrode is normally composed of carbon-supported noble metal catalyst such as Pt-Ru. The carbon support provides several desired functions. First, it enables the uniform dispersion of Pt-Ru particles on electrode substrate. Second, it provides electronic continuity. Carbon as a support has good chemical and electrochemical stabilities within the range of operational voltage, and thus it is popular as fuel cell catalyst support. The aim of the present investigation is to study the corrosion behavior of Pt-Ru/C at a loading of 1 mg/cm^2 on treated carbon paper in the presence of different concentration of ethanol in agitated condition as found during operation of a DEFC. Agitation occurs due to continuous flow of fuel through the channels of ribbed mono-polar plate (or bi-polar plate) in the case of single cell DEFC (or DEFC stack).

Experimental

Materials

The catalysts were used to prepare the working electrode was Pt-Ru (40%:20% by wt.)/C (Johnson Matthey Inc., UK). The size of the Pt-Ru/C catalyst particles were in the range of 10-16 nm. The carbon paper (Lydall 484C-1, USA) was used as a substrate for catalyst powder. Carbon (Vulcan XC72R) obtained from Cabot, USA was used as primary substance for preparation of catalyst ink. A mixture of Nafion$^®$ (SE-5112, Dupont USA) and isopropanol (Merck) was used as a binder for working electrode preparation. The mixture of ethanol (Merck), a fuel for DEFC, and dilute sulfuric acid (Merck) solution, as an electrolyte, were used as corrosion environment.

Preparation of the working electrode

At first, base for the catalyst ink (slurry) was prepared by dispersing given amount of activated carbon in isopropanol using ultrasonic water bath for 30 min. The prepared slurry was uniformly spread on an area of 2 x 2 cm^2 in the middle of a larger carbon paper of size 3 x 3 cm^2. It was then dried in an oven for 1 h at 100° C. The weight of dried electrode was measured and it was stored in plastic bag. The required quantity of Pt-Ru (40%:20% by wt.)/C catalyst powder was dispersed in mixture of Nafion (4 μl) and isopropanol (5 μl) 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 2 x 2 cm^2 carbon layer previously formed on the surface of the carbon sheet. The electrode was dried in an oven for 1 h at 100° C. The weight of the dried electrode was measured accurately to ensure that 4 mg of the catalyst spread on the surface of the electrode (equivalent loading of 1 mg/cm^2).

Experimental set-up and method

An electrode holder was fabricated to hold the working electrode (WE) as shown in fig. 1. The working electrode holder was made of two circular perspex disks. The WE was sandwiched between the two disks. The top disk, having opening of 2x2 cm^2 with a depth of 1 mm, allowed the working electrode to come in contact with corrosive environment (ethanol and H$_2$SO$_4$ electrolyte). Teflon tape was used to prevent the contact between uncoated catalyst surface of the working electrode and the electrolyte. The electrode holder with working electrode was kept in the bottom of a jacketed vessel containing three-electrode cell assembly as shown in fig. 2. The three-electrode cell assembly consists of platinum counter electrode, Ag/AgCl (sat. KCl) reference electrode and working electrode (Pt-Ru (40%:20% by wt.)/C). A glass stirrer was kept to avoid the effect of diffusion during corrosion study. Three-electrode cell assembly was connected to a potentiostat/galvanostat (Autolab PGSTAT30). Hot water was circulated through outer jacket to maintain temperature at 80° C. The corrosion study was carried out for Pt-Ru (40%:20% by wt.)/C catalyst in different concentration of ethanol i.e., 1 M and 5 M in acidic medium of 0.5 M H$_2$SO$_4$ at 80° C and at different agitator speed e.g., 250, 750 and 1500 RPM. The corrosion rate at different operating conditions was estimated from Tafel slope using software of potentiostat/galvanostat (Autolab PGSTAT30).

Results and Discussion

According to Faraday's law, there is a linear relationship between the metal corrosion rate and corrosion current,

$$R_M = \frac{M}{nF\rho} i_{corr} \qquad (2)$$

Where, R_M is the corrosion rate in μm/y, M is the atomic weight of metal, ρ is the density of metal, n is the charge number, which indicates the number of electrons exchanged in the reaction and F is the Faraday constant (96,485 C/mol). The Tafel slope of Pt-Ru (40%:20% by wt.)/C catalyst for ethanol oxidation is shown in fig. 3, from which corrosion rate can be calculated using eq. (2). The calculated corrosion rate values are tabulated in table 1. The corrosion rate increases with increasing the concentration of ethanol from 1M to 5M at different agitator speed e.g., 250, 750 and 1500 RPM. This behavior indicates that the electrochemical reaction is under the effect of concentration polarization following eq. (3) (Fontana and Greeve [6], Uhlig [7], Revie [8], Bard and Faulkner [9]),

$$\eta = \pm \beta \log(1 - i / i_L) \qquad (3)$$

Where, η is the overpotential, β is Tafel slope (= 2.3 RT / (α n F)), i_L is the limiting diffusion current (= n F k C_b), k is the mass transfer coefficient and C_b is the bulk ethanol concentration. The electrochemical oxidation reaction of ethanol 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. Similar observation was made by Lee and Park [10] on corrosion of ruthenium in ceric ammonium nitrate and nitric acid environment.

The stereomicroscopic analysis for the Pt-Ru (40%:20% by wt.)/C catalyst surface is shown in fig. 4. Fig. 4 (a) shows the uniform surface of Pt-Ru (40%:20% by wt.)/C catalyst before exposed to ethanol environment. The photomicrograph of the same surface, when exposed to 1 M ethanol, 0.5 M H_2SO_4 for 1 h at 80° C and at 1500 RPM, is shown in fig. 4 (b). Fig 4 (b) shows severely corroded areas and loss of mass after exposure to the corrosive environment of 1 M ethanol in 0.5 M H_2SO_4 at 80° C. This is clear evidence of corrosion on the surface of the Pt-Ru/C catalyst layer used in similar to DEFC environment.

Conclusions

The corrosion behavior of Pt-Ru (40%:20% by wt.)/C catalyst layer in two different ethanol concentrations and various agitator speed at 80° C is studied. The corrosion rate of Pt-Ru/C

catalyst increased with the increase in ethanol concentration from 1 M to 5 M and with the agitator speed from 250 to 1500 RPM. The observation of photomicrograph of Pt-Ru/C catalyst coated on carbon paper after exposure to 1 M ethanol and 0.5 M H_2SO_4 at 80 ^{o}C shows corrosion mark and loss of catalyst from the carbon paper. This clearly indicates Pt-Ru/C anode in DEFC is under galvanic corrosion and would degrade during DEFC operation.

Acknowledgement

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Table 1. Corrosion rate of Pt-Ru/C catalyst at 80 ^{o}C in different ethanol concentration and in 0.5 M H_2SO_4
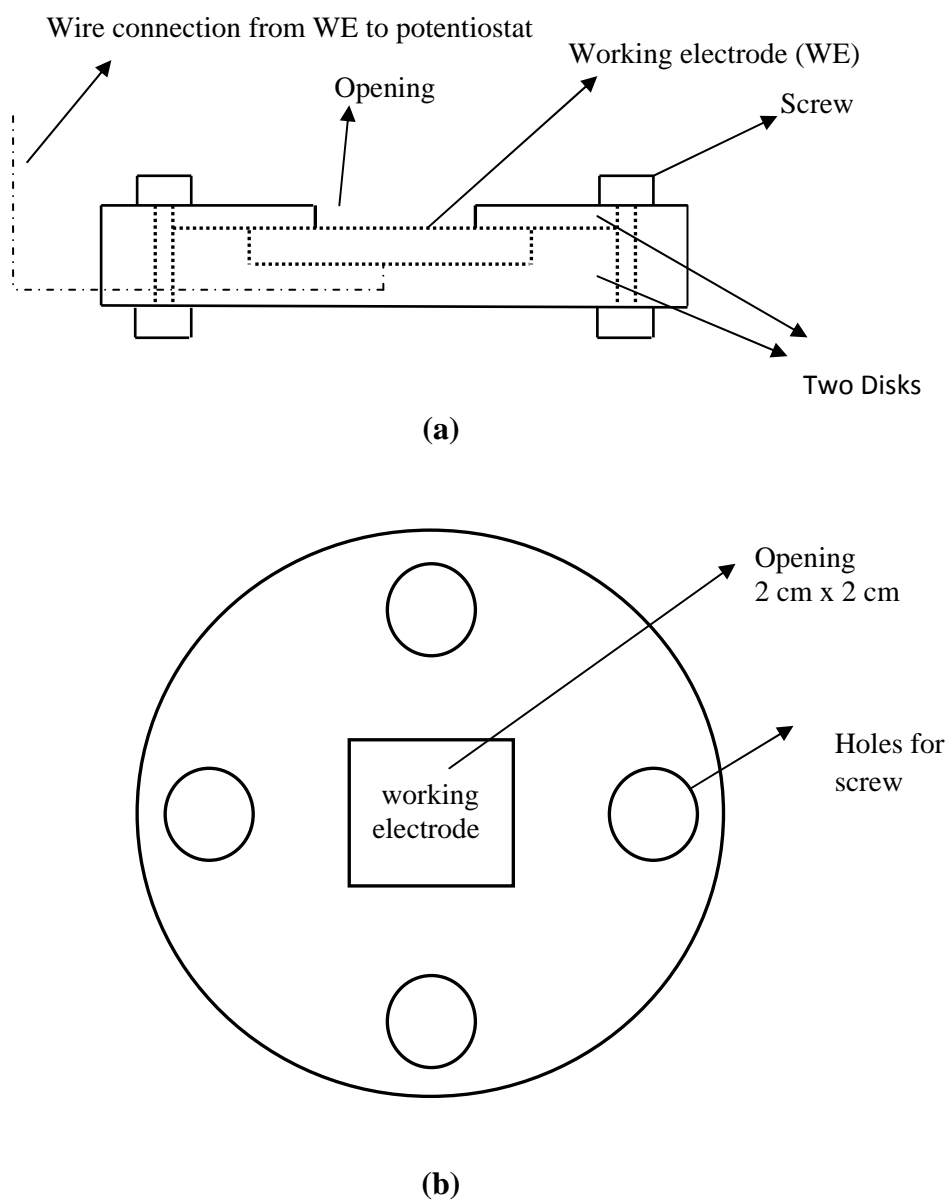
List of Figure Captions

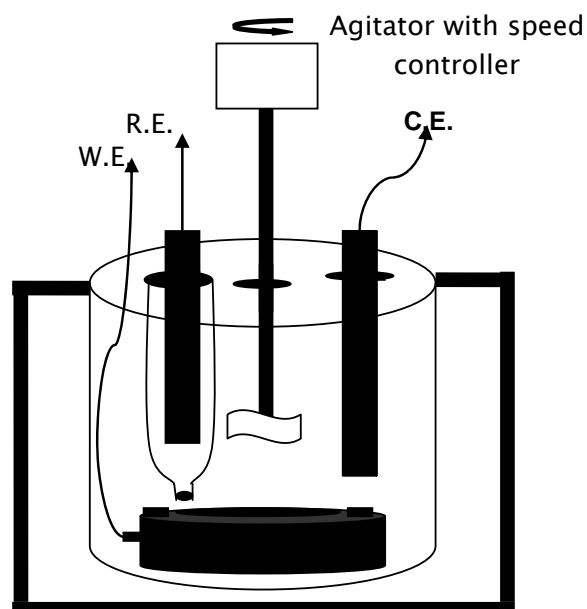Fig.1 Electrode holder (a) side view (b) plan view

Fig. 2 Experimental set-up for corrosion measurement cell. Working electrode = W.E., Counter electrode = C.E., Reference electrode = R.E.

Fig. 3 Tafel slop of Pt-Ru (40%:20% by wt.)/C at 1 M and 5 M concentration of ethanol and in 0.5 M H_2SO_4 at different agitator speeds e.g., 250, 750 and 1500 RPM

Fig.4 (a) Pt-Ru/C electrode before exposed to ethanol (b) Pt-Ru/C electrode after exposed to 1 M ethanol in 0.5 M H_2SO_4 for 1 h at 80 °C at 1500 RPM

Table 1. Corrosion rate of Pt-Ru/C catalyst at 80 ^{o}C in different ethanol concentration and in 0.5 M H_2SO_4

Ethanol Conc.	Agitator speed, RPM	Corrosion Rate, μm/y
1M	250	21.8
	750	17.48
	1500	31.7
5M	250	27
	750	51
	1500	36

(a)

(b)

Fig.1 Electrode holder (a) side view (b) plan view

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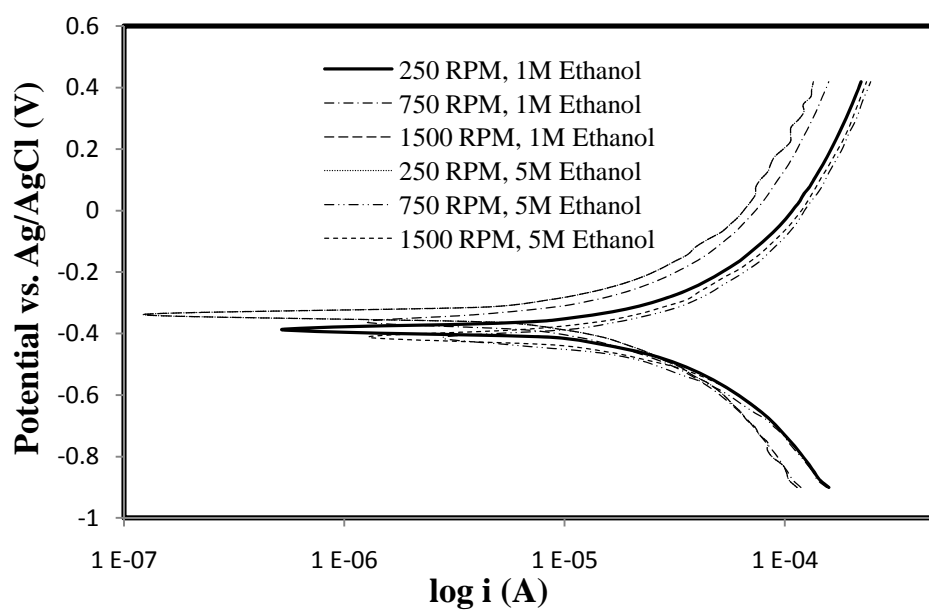
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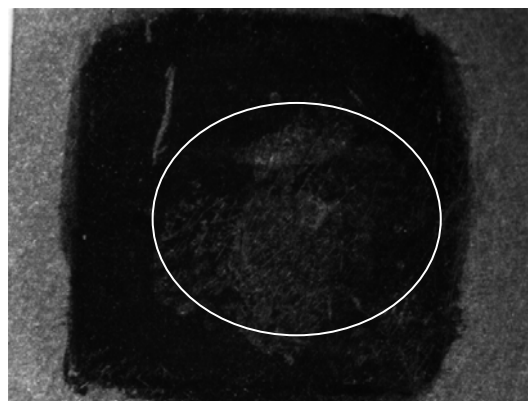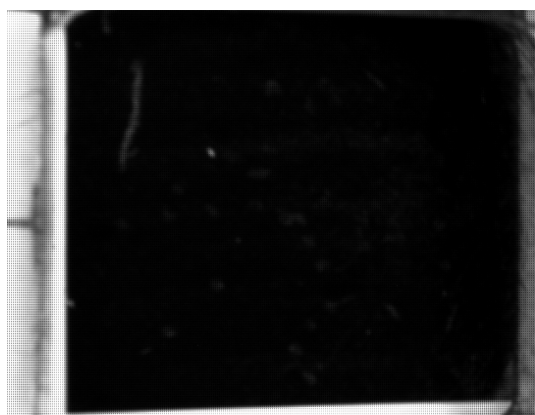
Fig.4 (a) Pt-Ru/C electrode before exposed to ethanol (b) Pt-Ru/C electrode after exposed to 1 M ethanol in 0.5 M H$_2$SO$_4$ for 1 h at 80 °C at 1500 RPM