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Evaluation of Catalytic Activity of Pt and Pt-Ru Catalysts for Electro-oxidation of Methanol in Acid Medium by Cyclic Voltammetry

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Abstract

The cyclic voltammetric study on the electro-oxidation of methanol on 30 % Pt and 20 % Pt +10 % Ru catalysts supported on Vulcan XC-72 was carried out in 0.5 M H_2SO_4. Kinetic parameters such as exchange current density, Tafel slope and heterogeneous rate constants were calculated. The 30 % Pt showed a higher apparent catalytic activity for the electro-oxidation of methanol as compared with 20 % Pt + 10 % Ru catalyst. The presence of Ru did not contribute significantly towards the apparent catalytic activity of a catalyst for the electro-oxidation of methanol but it may be useful to prevent the catalyst from CO poisoning. Thermodynamic parameters, ΔH^*, ΔS^*, and ΔG_{298}^* have been evaluated. The values of ΔH^* and ΔG_{298}^* were positive showing that the electro-oxidation of methanol is an endothermic and non-spontaneous process.

Keywords: methanol, acid medium, cyclic voltammetry, catalytic activity, kinetics, thermodynamic.

Introduction

The world fossil fuel sources are becoming scarce and the cost of the fuel is increasing. The extensive use of fossil fuels is also causing environment pollution and global warming problems. Fuel cell is a good technological option for solving energy and pollution problems [1]. Polymer electrolyte membrane fuel cells (PEMFC) have been investigated as high-density power sources in automobiles and in microelectronics [2, 3]. The efficiency of fuel cells depends on the catalytic activity of the catalysts. Use of methanol as fuel is getting popular because it is a liquid, which can be easily stored and handled.

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Development of direct methanol fuel cells (DMFC) requires catalysts with better electrocatalytic properties for the electro-oxidation of methanol and with better cell performance [4-6]. The reaction mechanism of the electro-oxidation of methanol has been extensively studied but still information about the kinetics of the electro-oxidation of methanol, temperature dependence and evaluation of catalytic activities from cyclic voltammetric behavior of the electro-oxidation of methanol are scarce.

The fabrication of membrane electrode assembly (MEA) for the evaluation of catalytic activity of different catalysts during fuel cell operation is a lengthy process [7-9]. Moreover, some catalysts may show poor performance during operation of fuel cells and as a result many of the MEAs may get wasted. Hence this practice of evaluation of performance of fuel cell catalysts appears costly. Due to these reasons, it is desirable to have certain techniques for evaluation of the catalytic activity of different fuel cell catalysts prior to their utilization in the fabrication of MEAs. Different alternate techniques are being used in this respect, e.g. scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-rays diffractometry (XRD), cyclic voltammetry, etc. [10-14]. Cyclic voltammetry is a well-established technique for the study of kinetics and mechanism of electron transfer processes [15-18]. It has been used by some people for the kinetic study of electro-oxidation of methanol and evaluation of catalytic activities of fuel cell catalysts [13, 14, 19-22].

Complete electro-oxidation of methanol in DMFC gives six electrons and six protons, as shown by the following reaction [23]:

$$CH_3OH + H_2O \rightleftarrows CO_2 + 6H^+ + 6e^- \qquad (1)$$

The protons (H^+ ions) pass through the polymer electrolyte membrane to the cathode side, while the electrons pass via external load to the cathode side to complete the circuit. Nafion® membrane is being used as polymer electrolyte membrane in PEMFC and DMFC. Nafion® membrane has an acidic nature and the conduction of protons through the membrane occurs via ion exchange process [1-3]. Due to the acidic nature of Nafion® membrane, many features are common in PEMFC and DMFC and hence the investigation of catalytic activity of different catalysts in acidic medium may give valuable information about the performance of a given catalyst in a PEMFC and DMFC.

The present study was made in connection with the preparation of high performance MEAs of PEMFC. The performances of two different catalysts containing 30 % Pt and 20 % Pt +10 % Ru supported on Vulcan XC-72 were evaluated on the basis of kinetic and thermodynamic data for the electro-oxidation of methanol in 0.5 M H_2SO_4 by using cyclic voltammetry. Various kinetic parameters such as real surface area, roughness factor, exchange current density, Tafel slope, heterogeneous rate constants and thermodynamic parameters have been evaluated and compared.

Experimental

Apparatus

A model 173 potentiostat/galvanostat, model 179 digital coulometer, model 175 universal programmer, model 178 electrometer probe and model RE 0089 x-y recorder, all from EG&G Princeton Applied Research (PAR), New Jersey, USA, were used for cyclic voltammetric measurements. Ultrasonic Cleaner, Model 08894-26, Cole-Parmer, USA, was used for ultrasonic mixing of a catalyst suspension.

The electrochemical cell consisted of a platinum working electrode, a platinum gauze as counter electrode and Ag/AgCl (sat. KCl) as reference electrode. All potentials throughout this paper were measured against Ag/AgCl (sat. KCl) reference electrode, but they are quoted with respect to the reversible hydrogen electrode for convenience.

Preparation of working electrodes

Two different Vulcan XC-72 supported catalysts containing 20 % Pt +10 % Ru and 30 % Pt, supplied by ***GasHub*** Technology Pte Ltd, Singapore, were used at working electrode. The catalysts were pasted onto the surface of graphite rod (Ø=1.0 cm) for cyclic voltammetric measurements. The graphite rod was insulated from the sides by using epoxy resin. The 8 mg mL^{-1} suspension of the given catalyst was prepared in deionized water by ultrasonic mixing and then 30 μL of the suspension were pipette out and spread over the graphite surface followed by application of 20 μL Nafion® solution (5 wt. %) that was used as a binder. The catalyst coating was dried at 30 °C.

Chemicals and materials

All the chemicals were analytical grade. Since there are well-developed methods for preparation of fuel cell catalysts [6, 13, 24-26], as received commercial catalysts were utilized for cyclic voltammetric characterization. All solutions were prepared in deionized water. Before each measurement, the working solution was purged with nitrogen gas. The electrochemical cell was placed in thermostated water bath for controlling the temperature of the working solution. All experiments were carried out at 25 °C except when measuring the thermodynamic parameters.

Results and discussion

Real surface area measurement

The real surface area was evaluated from the cyclic voltammogram by measuring the hydrogen adsorption charge in the same manner as reported elsewhere [19]. It is obvious from the cyclic voltammograms shown in Fig. 1 that the hydrogen adsorption charge on 20 % Pt + 10 % Ru catalyst is significantly low as compared with that on 30 % Pt catalyst. Such difference between hydrogen adsorption region of Pt and Pt-Ru catalysts has also been observed by other authors and is attributed to the presence of Pt-Ru alloy [27, 28]. The real surface area was calculated by using the following relation [29-32]:

$$S_{Pt\text{-}H} = \frac{Q_{Pt-H}\ \mu C}{210\ \mu C\, cm^{-2}} \qquad (2)$$

where $Q_{Pt\text{-}H}$ is the charge corresponding to hydrogen adsorption which may occur in the potential range 0.4 to 0.05 V vs. RHE in the cathodic sweep, and 210 μC is a generally accepted value for the charge transferred per cm^2 for monolayer hydrogen adsorption (Pt:H =1:1) on an ideal surface of polycrystalline platinum electrode having a roughness factor of one.

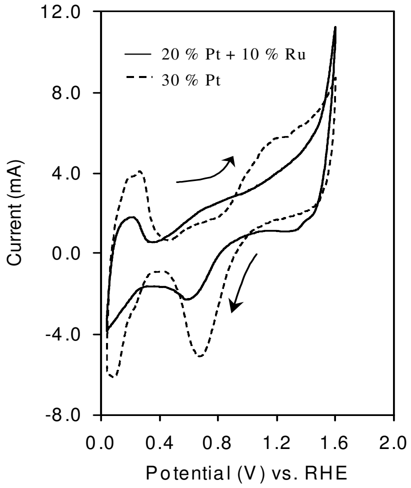

Figure 1. Comparison of the hydrogen adsorption region of the cyclic voltammogram of 30 % Pt and 20 % Pt + 10 % Ru catalysts at 50 mV s^{-1}scan rate in 0.5 M H_2SO_4.

The roughness factor "R.F" of a catalyst was calculated by using the following relation [32, 33]:

$$R.F = \frac{\text{Real surface area}}{\text{Apparent surface area}} \qquad (3)$$

This relation shows that the value of roughness factor is equal to one when the real surface area of an electrode is exactly equal to its apparent surface area.
The data given in Table 1 show that the real surface area and roughness factor of the 30 % Pt catalyst is higher as compared to that of 20 % Pt + 10 % Ru catalyst.

Table 1. Surface area and roughness factor data of 30 % Pt and 20 % Pt + 10 % Ru catalysts evaluated from the hydrogen adsorption charge measured from cyclic voltammogram in the potential range 0.4 to 0.05 V vs. RHE in the cathodic sweep at 50 mV s^{-1} in 0.5 M H_2SO_4.

Type of catalysts	Apparent surface area (cm^2)	Real surface area (cm^2)	Roughness factor (R.F)
20 % Pt + 10 % Ru	0.785	24.44 ± 0.67	31.13 ± 0.85
30 % Pt	0.785	70.69 ± 1.70	90.05 ± 2.17

Characteristic features of the electro-oxidation of methanol

Fig. 2 shows the cyclic voltammograms of Pt and Pt-Ru catalysts in 0.5M H_2SO_4. Both catalysts show almost the same characteristic features for the electro-oxidation of methanol. In the anodic sweep, the electro-oxidation of methanol gives a well-defined anodic peak "Peak-I" which appears at almost the same potential of 0.94 V on both catalysts. From the comparison of Fig. 1 and Fig. 2, it is obvious that Peak-I appears at the potential which is equivalent to the onset potential of compact hydrous oxides and other oxides. In the subsequent cathodic sweep, the electro-oxidation of methanol recommences just after the reduction of O-electroadsorbed species and gives rise to a reverse anodic peak, "Peak-II". The peak potential of the reverse anodic peak was dependent on oxide coverage of the catalyst and was shifted in the cathodic potential direction with increasing anodic potential limit. The appearance of anodic peaks for the electro-oxidation of methanol in both anodic and cathodic sweep has been attributed to the high catalytic activity of Pt based catalysts for the electro-oxidation of methanol. It also indicates that the electro-oxidation of methanol on Pt-electrocatalysts is an irreversible electron transfer process.

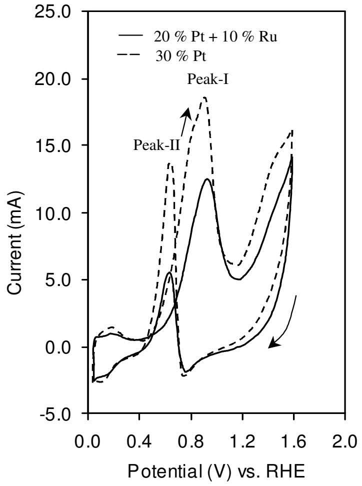

Figure 2. Comparison of the cyclic voltammogram of 30 % Pt and 20 % Pt + 10 % Ru catalysts in 0.2 M CH_3OH + 0.5M H_2SO_4 at 50 mV s^{-1} scan rate.

It is also obvious from Fig. 2 that the hydrogen adsorption region is greatly suppressed during electro-oxidation of methanol on 30 % Pt catalyst and becomes almost equal to that of 20 % Pt + 10 % Ru catalyst. This behavior may be attributed to the blocking of the active sites of Pt catalyst by CO, which may be produced as intermediate during incomplete electro-oxidation of methanol. The less suppression of hydrogen adsorption region of 20 % Pt +10 % Ru catalyst during electro-oxidation of methanol may be due to its greater tolerance to the CO poisoning. The role of Ru in Pt-Ru catalysts has been recognized by many authors due to dual function of Pt-Ru catalyst, i.e., the adsorption of methanol molecules by the Pt atoms and the adsorption of oxygen containing species such as H_2O by the Ru atoms [34-36]. The Ru atoms adsorb the H_2O

molecules at a potential as low as 0.2 V and contribute towards the carbon monoxide removal reaction according to the following reaction [28, 34-36]:

$$PtCO + RuOH \rightarrow Pt + Ru + CO_2 + H^+ + e^- \qquad (4)$$

It has been reported that CO oxidation begins at lower anodic potential on Pt-Ru catalyst and at higher anodic potential on Pt catalyst [37, 38]. Due to lower onset potential for CO oxidation, the Pt-Ru catalyst becomes more tolerant to the CO poisoning.

Evaluation of catalytic activity of a catalyst from polarization curves

Polarization curves, plots of electrode potential against the logarithm of current density, are drawn for evaluation of kinetic parameters such as exchange current density and Tafel slope (slope of plot of E vs. log i). A more catalytically active catalyst may be identified from the polarization curves by using the fact that it gives the highest current density at any given potential for a given electrochemical reaction. The exchange current density and Tafel slope are evaluated from the polarization curves on the basis of Tafel equation which for an anodic process can be written as [33]:

$$\eta = b \log \frac{i}{i^o} \qquad (5)$$

where b is the Tafel slope (in V decade^{-1}), i is the apparent current density (in mA cm^{-2}), i^o is the exchange current density (in mA cm^{-2}) at the reversible potential of a given electrode reaction, and η is the overpotential, i.e., departure of an electrode potential from the reversible potential of a given electrode reaction. The overpotential "η" may be represented by the following relation:

$$\eta = E - E_r \qquad (6)$$

where E is taken as electrode potential (in V) and E_r is the reversible potential. The value of b is given by the following relation:

$$b = \frac{2.303\, R\, T}{\alpha n_a F} \qquad (7)$$

where αn_a is the product of an electron transfer coefficient and number of electrons transferred in rate determining step, F is the Faraday's constant, T is the absolute temperature and R is the universal gas constant.

Since the process of the electro-oxidation of methanol on platinum based catalysts is an irreversible process, the evaluation of an exact value of the reversible potential "E_r" from cyclic voltammetric data is difficult. The value E_r is required for evaluation of exchange current density on the basis of Eq. (5). In order to avoid such difficulty, the following relation was derived from Eq. (5) after the substitution of η value from Eq. (6):

$$E = a + b \log i \qquad (8)$$

where

$$a = E_r - b \log i^o \qquad (9)$$

Eq. (8) is a linear equation and hence one may evaluate the constants “a” and “b” from the slope and intercept of the plot of E vs. log i, respectively. The current-potential data for drawing the polarization curves were obtained from the analysis of the rising portion of the forward anodic peak of the electro-oxidation of methanol. The polarization curves shown in Fig. 3 indicate that at any given potential, the value of log i is higher on 30 % Pt catalyst as compared with that on 20 % Pt + 10 % Ru catalyst. In other words, 30 % Pt catalysts have a higher catalytic activity for the electro-oxidation of methanol. It is also obvious from the polarization curves that a given value of log i may be obtained at lower anodic potential on 30 % Pt catalyst, and at a slightly higher potential on 20 % Pt + 10 % Ru catalyst. This lower value of anodic potential for getting a given value of log i may also be used as criteria for indication of higher catalytic activity of a catalyst.

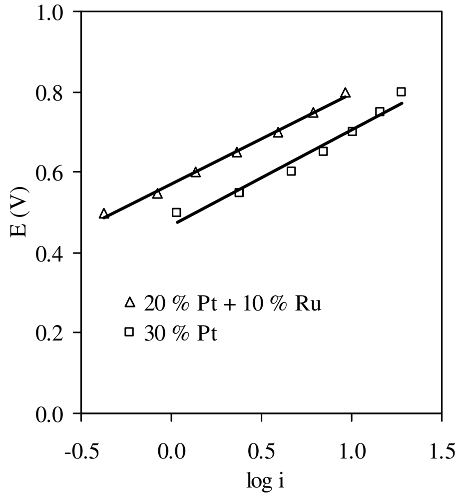

Figure 3. Polarization curves for the electro-oxidation of 0.2 M CH_3OH in 0.5 M H_2SO_4 on 30 % Pt and 20 % Pt + 10 % Ru catalysts. The current-potential data were obtained from the analysis of the rising portion of forward anodic peak of the electro-oxidation of 0.2 M CH_3OH in 0.5 M H_2SO_4 at 50 mV s^{-1} scan rate.

The values of Tafel slope, electron transfer coefficient and exchange current densities evaluated from the polarization curves are given in Table 2. The exchange current densities at 0.7 V were evaluated from the value of intercept “a” by putting E_r = 0.7 V. This value of E_r was used just for comparison of the kinetic data at a potential of interest to avoid the difficulty of evaluation of reversible potential from cyclic voltammetric data. This practice of comparison of kinetic data at a certain potential of interest has also been reported elsewhere [19, 28]. However, in such practices it may be necessary to report the values of both intercept and slope of the plot of E vs. log i curves, so that one may be able to re-calculate the exchange current densities for a given electrode process at any desired reference potential from the reported data. The comparison of the polarization data in Table 3 shows that the values of Tafel slope and electron transfer coefficient are nearly the same for both catalysts, while exchange current density is significantly high on 30 % Pt catalyst as compared with that of 20 % Pt + 10 % Ru catalyst.

Table 2. Polarization data obtained from the analysis of current-potential data of the rising portion of forward anodic peak of the electro-oxidation of 0.2 M CH_3OH in 0.5 M H_2SO_4 on 30 % Pt and 20 % Pt + 10 % Ru catalysts.

Type of catalysts	Intercept "a"	Tafel slope "b" (V decade^{-1})	αn_a	Exchange current density at 0.7 V "$i^o_{(0.7\ V)}$" (mA cm^{-2})
20 % Pt + 10% Ru	0.572	0.225	0.262	3.71
30 % Pt	0.465	0.239	0.247	9.62

Evaluation of catalytic activity from peak current data

The comparison of peak current data for the electro-oxidation of 0.2 M CH_3OH on Pt and Pt-Ru catalysts is given in Table 3. The data show that the catalytic activity of 30 % Pt catalyst is higher than that of 20 % Pt + 10 % Ru catalyst. It means that the presence of 10 % Ru does not enhance the catalytic activity of 20 % Pt up to that of 30 % Pt catalyst. It is assumed that a relatively higher percentage of Ru in the Pt based catalyst may result in significant improvement of the performance of a catalyst for the electro-oxidation of the methanol via oxidation of the CO from the adjacent Pt atoms. T. Kessler et al. [38] have reported that the presence of 30 % Ru is the most suitable amount for obtaining a high performance Pt-Ru catalyst for the electro-oxidation of methanol.

Table 3. Kinetic data for the electro-oxidation of methanol in 0.5 M H_2SO_4 on 30 % Pt and 20 % Pt + 10 % Ru catalysts.

Type of catalysts	E_p at 50 mV s^{-1} (V)	Peak current (mA)	log I_p / log υ	E_p/log υ (V decade^{-1})	$k_s \times 10^{-5}$ at 50 mV s^{-1} (cm s^{-1})
20 % Pt + 10% Ru	0.94	12.4	0.43	0.19	5.19 ± 0.38
30 % Pt	0.94	18.1	0.42	0.25	8.72 ± 0.59

Effect of scan rate on the peak current

The peak current for the electro-oxidation of methanol increased with increasing scan rates. The order of the increase of peak current with respect to scan rate was evaluated from the slope of the plot of logarithm of peak current "logI_p" versus the logarithm of scan rate "log υ", as shown in Fig. 4. The data in Table 3 show that in both cases the order of increase of peak current with increasing scan rate is close to 0.5. In other words, the peak current varies approximately linearly with square root of scan rate. It means that the process of electro-oxidation of methanol has the characteristics of a diffusion-controlled process [39, 40].

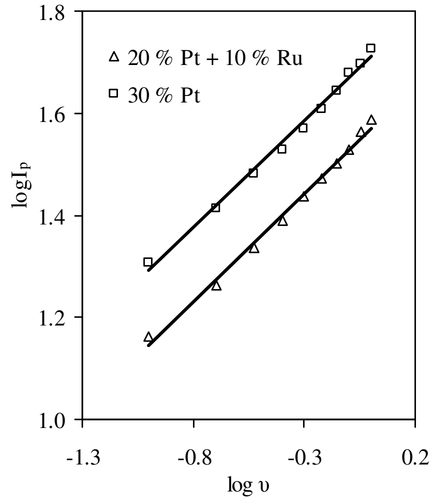

Figure 4. Plots of logarithm of peak current “$\log I_P$” vs. the logarithm of scan rate “log υ” for the electro-oxidation of methanol in 0.5 M H_2SO_4 on 30 % Pt and 20 % Pt + 10 % Ru catalysts.

Effect of scan rate on the peak potential

The peak potential of the forward anodic peak of cyclic voltammogram of the electro-oxidation of methanol shifted toward more anodic potential with increasing scan rate, as shown in Fig. 5, in term of plots of peak current versus logarithm of scan rates. The shift of peak potential with increasing scan rate is a characteristic property of an irreversible electron transfer process [33]. The data of slope of E_p vs. log υ given in Table 3 indicate that the magnitude of shift of peak potential with increasing scan rate is higher on 30 % Pt catalyst as compared with that on 20 % Pt + 10 % Ru catalyst.

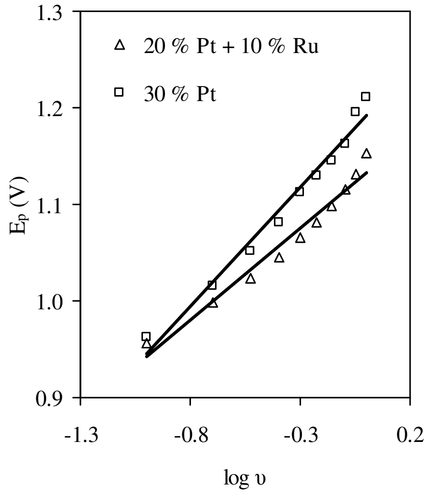

Figure 5. Plots of peak potential “E_P” vs. the logarithm of scan rate “log υ” for the electro-oxidation of methanol in 0.5 M H_2SO_4 on 30 % Pt and 20 % Pt + 10 % Ru catalysts.

Evaluation of heterogeneous rate constants

The study of kinetics of a reaction at an electrode surface is of great importance for basic understanding of the heterogeneous electron transfer processes [15-19, 39-41]. The heterogeneous rate constants "k_s" for the electro-oxidation of methanol on fuel cell catalysts may be evaluated by using the following relation between peak current and peak potential of a completely irreversible electrode reaction [19, 40]:

$$I_p = 0.227\, n\, F\, A\, C\, k_s \exp\left[\frac{\alpha n_a F}{RT}(E_p - E^o)\right] \tag{10}$$

where I_p is the peak current (in Amperes, A), n is the total number of electrons transferred in overall reaction (in this case 6), F is the Faraday's constant, A is the apparent surface area of the electrode (in cm^2), and C is the bulk concentration of the reactant (in mol cm^{-3}). The other parameters have their usual meanings.

On rearranging Eq. (10), we get

$$k_s = \frac{I_p}{0.227\, n\, F\, A\, C} \exp\left[\frac{-\alpha n_a F}{RT}(E_p - E^o)\right] \tag{11}$$

This equation was used for the evaluation of heterogeneous rate constant. Since the electro-oxidation of methanol is an irreversible process, it is difficult to measure the standard electrode potential "E^o" for the electro-oxidation of methanol from cyclic voltammetric data. For convenience the value of E^o was taken 0.7 V for reference purpose as in case of polarization measurements.

The values of k_s were numerically calculated from Eq. (11) using experimental values of I_p, E_p, and αn_a obtained from the analysis of forward anodic peak at 50 mV s^{-1} scan rate. Comparison of the data in Table 3 shows that the heterogeneous rate constant for the electro-oxidation of methanol is higher on 30 % Pt catalyst and hence the utilization of 30 % Pt catalysts in the fabrication of MEAs for fuel cells may give a comparatively higher apparent current density. The presence of Ru in the Pt-Ru catalyst may be appreciated only for its role in the removal of CO from the adjacent Pt atoms as mentioned in previous sections.

Thermodynamic studies

The effect of temperature on the heterogeneous rate constant was also investigated. The heterogeneous rate constant for the electro-oxidation of methanol increased with increasing temperature. The thermodynamic parameters were calculated using the relation based on Marcus theory [41], which may be expressed in simpler form for one mole of a reacting species as [18, 19]

$$\ln\left(\frac{k_s}{Z_{het}}\right) = \frac{-\Delta H^*}{RT} + \frac{\Delta S^*}{R} \tag{12}$$

where Z_{het} is the collision number for heterogeneous electron transfer process and its value can be calculated at any given temperature using the following relation [41]:

$$Z_{het} = \left(\frac{RT}{2\pi M}\right)^{1/2} \tag{13}$$

where M is the molecular mass of the reacting species and the other terms have usual meanings.

The values of ln k_s/ Z_{het} for both catalysts were calculated at different temperatures and were plotted against 1/T, as shown in Fig. 6. The values of ΔH^* and ΔS^* were obtained from the slope and intercept of the plot of ln k_s/ Z_{het} vs. 1/T, respectively. The values of free energy of activation at 298 K "ΔG_{298}^*" were calculated from the values of ΔH^* and ΔS^* using the following relation:

$$\Delta G^* = \Delta H^* + T\Delta S^* \tag{14}$$

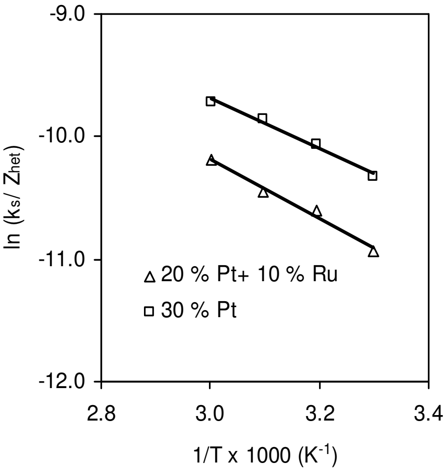

Figure 6. Plots of ln k_s/Z_{het} vs. 1/T for evaluation of thermodynamic parameters of the electro-oxidation of methanol in 0.5 M H_2SO_4 on 30 % Pt and 20 % Pt + 10 % Ru catalysts.

The comparison of thermodynamic data for the electro-oxidation of methanol on different fuel cell catalysts is made in Table 4. The values of ΔH^* were positive in both cases which indicates that the process of the electro-oxidation of methanol on fuel cell catalysts is an activation controlled process and hence their catalytic activities may be increased significantly by increasing the temperature of the fuel cell. The values of ΔG_{298}^* were also positive and were nearly the same for both catalysts. The positive values of ΔG_{298}^* indicate that the electro-oxidation of methanol on fuel cell catalysts is an endothermic and non-spontaneous process.

Table 4. Thermodynamic data for the electro-oxidation of methanol on 30 % Pt and 20 % Pt + 10 % Ru catalysts.

Type of catalysts	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	$\Delta G_{298}{}^*$ (kJ mol^{-1})	Correlation coefficient "R^2"
20 % Pt + 10% Ru	20.05	-24.59	27.36	0.984
30 % Pt	17.14	-29.22	25.81	0.989

Conclusions

Cyclic voltammetric study of the electro-oxidation of methanol on 30 % Pt and 20 % Pt +10 % Ru catalysts supported on Vulcan XC-72 was carried out in 0.5 M H_2SO_4 to find various kinetic and thermodynamic parameters. The hydrogen adsorption region of 30 % Pt catalysts was suppressed significantly in the presence of methanol, which was attributed to the blocking of the active sites of Pt particles by the formation of adsorbed intermediate species like CO. The rate of electro-oxidation of methanol was higher on 30 % Pt as compared with that on 20 % Pt + 10 % Ru catalyst. The role of Ru in Pt-Ru catalysts was recognized only for its participation in the CO removal reaction. The electro-oxidation of methanol was an endothermic and non-spontaneous process and hence higher temperature is more favorable for increasing the rate of electro-oxidation of methanol on fuel cell catalysts.

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