

Electro-oxidation of Methanol on Fuel Cell Catalysts and Evaluation of their Catalytic Activities by Cyclic Voltammetry

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Summary: The electro-oxidation of methanol on smooth Pt-strip and 10 % Pt supported on Vulcan XC-72 was studied in acidic medium using cyclic voltammetry. The electro-oxidation of methanol gave well-defined anodic peaks in both anodic and cathodic sweeps. Real surface area, roughness factor, exchange current density, peak current and the heterogeneous rate constant for electro-oxidation of methanol were found to be higher on 10 % Pt-catalyst as compared with smooth Pt-strip. The thermodynamic parameters, ΔH° , ΔS° and ΔG_{298}° were evaluated. The value of ΔH° for electro-oxidation of methanol on smooth Pt-strip was higher and found 57 kJ mol⁻¹, while the value of ΔH° on 10 % Pt-catalyst was 26 kJ mol⁻¹. The more positive value of ΔH° obtained on smooth Pt-strip was attributed to its poor catalytic activity for electro-oxidation of methanol. The values of ΔG_{298}° were also positive indicating that the electro-oxidation of methanol on fuel cell catalysts was an endothermic and non-spontaneous process and hence the higher temperature might be more favorable for increasing the catalytic activity of fuel cell catalysts.

Introduction

Electro-oxidation of methanol has been extensively studied mainly due to its possible use as a liquid fuel in the fuel cells [1, 2]. The efficiency of fuel cells depends on the catalytic activities of catalysts. Development of direct methanol fuel cells (DMFC) requires catalysts with better electrocatalytic properties for the electro-oxidation of methanol and with better cell performance [3]. Pt-Ru/C catalysts have been extensively investigated and are currently being used in DMFCs [4]. Although electrocatalytic reaction mechanism of methanol oxidation has been extensively studied [5-8] but still the information about the heterogeneous rate constants, temperature dependence and evaluation of catalytic activities of catalysts from the electro-oxidation methanol are scarce. Since cyclic voltammetry is a well-established technique for the study of kinetics and mechanism of electron transfer processes [9-11], it can be of great significance for the study of electro-oxidation of methanol and evaluation of catalytic activities of catalysts as well [8, 12-16].

The aim of this paper is to compare the catalytic activities of smooth Pt-strip and 10 % Pt catalyst supported on Vulcan XC-72 for methanol oxidation by cyclic voltammetry. Various parameters such as real surface area, roughness factor, the Tafel slope, exchange current densities, peak current,

heterogeneous rate constants and thermodynamic parameters have been evaluated and compared as well.

Results and Discussion

Real Surface Area Measurements

The real surface area is an area of a catalyst that is actually available for electrochemical reaction. It may be evaluated by determining the amount of charge transferred during adsorption of hydrogen on the surface of platinum catalyst ($Q_{\text{Pt-H}}$). The charge transferred for monolayer hydrogen adsorption (Pt:H = 1:1) on an ideal surface of polycrystalline platinum electrode having a roughness factor of one is considered to be 210 $\mu\text{C cm}^{-2}$ and hence the total real surface area of a given platinum catalyst ($S_{\text{Pt-H}}$) can be calculated by using the following relation [17-20]:

$$S_{\text{Pt-H}} = \frac{Q_{\text{Pt-H}} \mu\text{C}}{210 \mu\text{C cm}^{-2}} \quad (1)$$

Knowing the real surface area of the catalyst, one can calculate the roughness factor (R.F) by using the following relation [20, 21]:

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$$R.F = \frac{\text{Real surface area}}{\text{Apparent surface area}} \quad (2)$$

where apparent surface area is the usual geometric surface area of an electrode which may come in direct contact with the working solution. The eq. 2 shows that the value of roughness factor may be equal to one when the real surface area is exactly equal to an apparent surface area of an electrode.

The cyclic voltammogram of smooth Pt-strip at scan rate of 50 mV sec⁻¹ in 0.5 M H₂SO₄ is shown in Fig. 1 where the shaded area indicates the hydrogen adsorption region along with background correction. Since the charge (*Q*) is the product of current (*i*) and time (*t*), therefore, one may evaluate the total charge transferred during hydrogen adsorption by dividing the shaded area into large number of small areas of equal width and then calculating the sum of product of current and small change in time. The time may be evaluated from the scan rate which is 50 mV sec⁻¹ in this case i.e. an area of 50 mV along X-axis may be equal to one second. The comparison of the data of real surface area and the roughness factor of smooth Pt-strip and 10 % Pt catalyst is given in Table-1. The data show that the real surface area and the roughness factor of a few milligrams of 10 % Pt-catalyst are higher than those of the smooth Pt-strip, consequently the 10 % Pt-catalyst is expected to have higher catalytic activity for electro-oxidation of methanol as compared with smooth Pt-strip which is confirmed in next sections.

Table-1: Data of real surface area and roughness factor of smooth Pt-strip and 10 % Pt-catalyst.

Type of catalyst	Bulk mass of catalyst material (mg)	Mass of only Pt in the catalyst material (mg)	Apparent surface area (cm ²)	Real surface area (cm ²)	Roughness factor (R.F)
Smooth Pt-strip	525.2	525.2	3.04	7.05	2.32
10 % Pt-catalyst	0.24	0.024	0.79	24.51	31.03

Cyclic Voltammetric Characteristics of Platinum Catalysts during Methanol Oxidation

The cyclic voltammetric characteristics of smooth Pt-strip in the presence of 0.2 M CH₃OH in 0.5 M H₂SO₄ are shown in Fig. 2. In the anodic sweep the electro-oxidation of methanol gives a well-defined forward anodic peak (Peak-I) while in the subsequent cathodic sweep the electro-oxidation of methanol begins again and gives a reverse anodic peak (Peak-II). The appearance of only anodic peaks

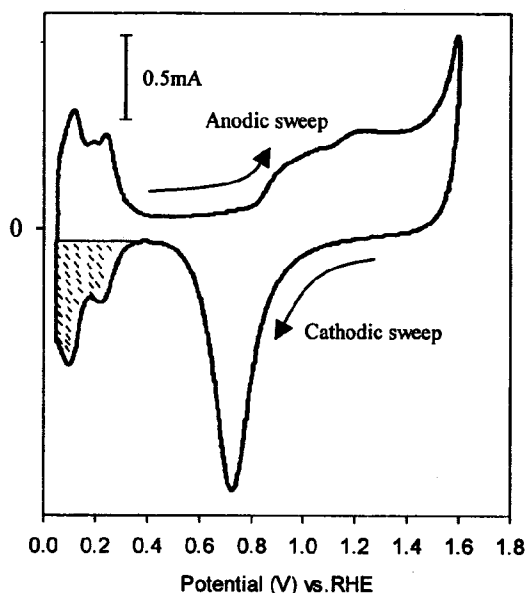


Fig. 1: Cyclic voltammogram of smooth Pt-strip at scan rate of 50 mV sec⁻¹ in 0.5 M H₂SO₄; shaded area shows the hydrogen adsorption region (the cathodic and anodic potential limits are 0.05 and 1.6 V against reversible hydrogen electrode (RHE) respectively).

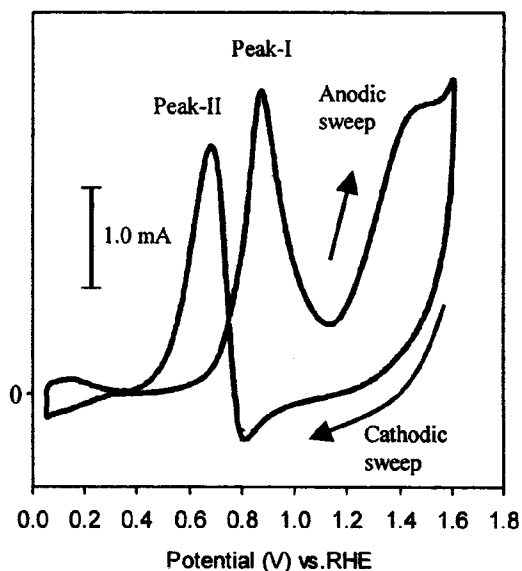


Fig. 2: Cyclic voltammogram of smooth Pt-strip in the presence of 0.2 M CH₃OH in 0.5 M H₂SO₄. The cyclic voltammetric conditions are same as in Fig.1.

in both anodic and cathodic sweeps indicates that electro-oxidation of methanol on platinum electrode is an irreversible electron transfer process which may occur via various intermediate steps as discussed elsewhere [12]. The cyclic voltammetric behavior of electro-oxidation of methanol on 10 % Pt-catalyst was almost the same as on smooth Pt-strip electrode and hence it is not discussed here in detail.

Comparison of the Polarization Curves

Comparison of the polarization plots *i.e.* potential (E) vs. the logarithm of the apparent current density ($\log i$) for electro-oxidation of methanol on smooth Pt-strip and 10 % Pt-catalyst is made in Fig. 3. Current-potential data were obtained by analyzing the forward anodic peak obtained in 0.5 M H_2SO_4 for 0.2 M CH_3OH at a scan rate of 50 mV sec^{-1} . 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. The data in Fig. 3 shows that a given current density may be obtained at significantly lower potential on 10 % Pt-catalyst as compared with smooth Pt-strip. In other words, 10 % Pt-catalyst is more catalytically active for methanol oxidation than smooth Pt-strip. The catalytic activities of catalysts may be best assessed by comparing the data of exchange current density that may be evaluated from the analysis of the following equation for an anodic polarization [22, 23]:

$$E = E_r - b \log i^0 + b \log i \quad (3)$$

where E is the measured potential (V), E_r is the reversible electrode potential, i is the apparent current density (mA cm^{-2}), i^0 is the exchange current density (mA cm^{-2}) at reference potential of E_r and b is the Tafel slope. Since E_r , b and i^0 are constants hence the eqn. 3 may be re-written as:

$$E = a + b \log i \quad (4)$$

$$\text{where } a = E_r - b \log i^0 \quad (5)$$

The eq. 4 is in the form of linear equation which may give positive value of b from the slope of the E vs. $\log i$ plots (Fig. 3). Since value of b indicates the magnitude of change in potential for each ten-fold change in current density, therefore, the unit of b may be represented as V decade^{-1} . The value of product of electron transfer coefficient and

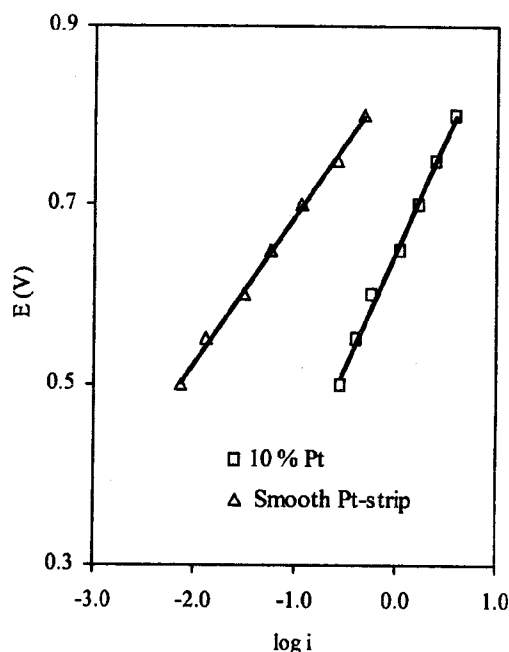


Fig. 3: Polarization curves for electro-oxidation of 0.2 M CH_3OH in 0.5 M H_2SO_4 at scan rate of 50 mV sec^{-1} on smooth Pt-strip and 10 % Pt-catalyst.

number of electrons involved in the rate determining step may be evaluated from the value of b using the following relation [23]:

$$b = 2.303 \frac{RT}{an_a F} \quad (6)$$

The value of i^0 may be evaluated from the intercept of the E vs. $\log i$ plots (Fig. 3) using eq. 4. The evaluation of i^0 may need the value of reversible potential (E_r) for electro-oxidation of methanol in a given supporting electrolyte (acidic medium in this case). Since the process of electro-oxidation of methanol at platinum electrode is a totally irreversible process giving only anodic peaks in both anodic and cathodic sweeps, therefore, the evaluation of reversible potential from the cyclic voltammetric data is difficult. In order to avoid such difficulties, a certain reference potential of interest has been used for comparison of kinetic data [12, 24]. In this paper, the kinetic data have been evaluated at 0.7 V, which lies along the way up the forward anodic peak.

The values of b and i^0 for electro-oxidation of methanol on smooth Pt-strip and 10 % Pt catalyst

are given in Table-2. The value of i^0 is significantly higher on 10 % Pt-catalyst as compared with smooth Pt-strip electrode. This higher value of i^0 obtained on 10 % Pt-catalyst indicates that electro-oxidation of methanol is catalytically more favorable on 10 % Pt-catalyst supported on carbon as compared with smooth Pt-strip.

Table-2: Polarization data for electro-oxidation of 0.2 M CH₃OH on smooth Pt-strip and 10 % Pt-catalyst in 0.5 M H₂SO₄ at scan rate of 50 mV sec⁻¹.

Type of catalyst	Intercept "a"	Tafel slope "b" (V decade ⁻¹)	an.	Exchange current density "i ⁰ " at 0.7 V (mA cm ⁻²)
Smooth Pt-strip	0.85	0.16	0.37	0.12
10 % Pt-catalyst	0.65	0.25	0.24	1.58

Comparison of Peak Current Data

The comparison of peak current data for electro-oxidation of 0.2 M CH₃OH on smooth Pt-strip and 10 % Pt-catalyst at scan rate of 50 mV sec⁻¹ is made in Table-3. The data show that the peak current for electro-oxidation of methanol is higher on 10 % Pt-catalyst as compared to that on smooth Pt-strip electrode. The higher peak current obtained for electro-oxidation of methanol on 10 % Pt-catalyst may be attributed to its higher surface area and roughness factor as compared with smooth Pt-electrode.

Effect of Scan Rate on the Peak Current

The peak current of the methanol oxidation increases with increasing scan rates. The data in Fig. 4 shows that for all scan rates the log I_p is higher for 10 % Pt-catalyst as compared with smooth Pt-strip electrode. The order of the increase of peak current with respect to scan rate was evaluated from the slope of the plot of log I_p vs. log v , where v is the scan rate and found to be close to 0.5 in both cases as may be expected for a diffusion-controlled process [23].

Effect of Scan Rate on the Peak Potential

The peak potential of the forward anodic peak of methanol electro-oxidation shifted towards higher anodic potential with increasing scan rate as shown in Fig. 5. The shift of peak potential with increasing scan rate indicates that the electro-oxidation of methanol is an irreversible electron transfer process.

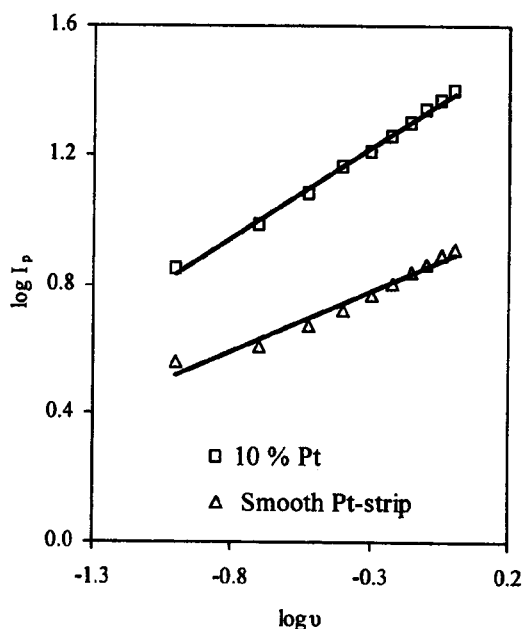


Fig. 4: Plots of logarithm of peak current density (log I_p) against logarithm of the potential scan rate (log v) for smooth Pt-strip and 10 % Pt-catalyst.

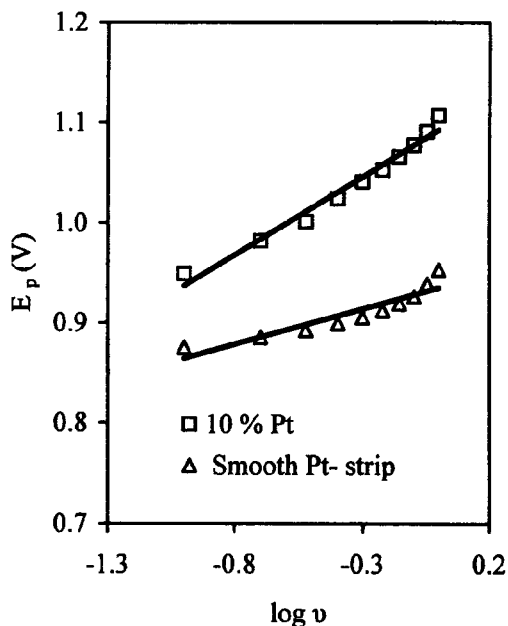


Fig. 5: Plots of peak potential (E_p) against logarithm of potential scan rate (log v) for smooth Pt-strip and 10 % Pt-catalyst.

Evaluation of Heterogeneous Rate Constant

Kinetic study of a reaction on the surface of an electrode is of great significance for basic understanding of the heterogeneous electron transfer processes [23, 25-27]. The heterogeneous rate constant (k_s) for the electro-oxidation of methanol on different fuel cell catalysts may be evaluated by using the following relation for an anodic process involving total n -electrons in the overall reaction [25]:

$$I_p = 0.227nFAC k_s \exp\left[\frac{an_a F}{RT}(E_p - E^0)\right] \quad (7)$$

where I_p is the peak current (taken in amperes, A), n is the total number of electrons transferred in overall reaction (in this case 6), A is the apparent surface area of an electrode (in cm^2), C is the bulk concentration of the reactant (in mol cm^{-3}) and k_s is the standard heterogeneous rate constant for electro-oxidation of methanol. The other factors have their usual meanings. On rearranging eq. 7, we get

$$k_s = \frac{I_p}{0.227nFAC} \exp\left[\frac{-an_a F}{RT}(E_p - E^0)\right] \quad (8)$$

Equation 8 may be used for evaluation of heterogeneous rate constant for a totally irreversible electron transfer reaction. Since electro-oxidation of methanol at Pt-electrode is a totally irreversible process, therefore, it is difficult to measure the standard electrode potential (E^0) for electro-oxidation of methanol from cyclic voltammetric data. For convenience the value of E^0 was taken 0.7 V for reference purpose as in case of polarization measurements.

The values of k_s were numerically calculated from eq. 8 using the data of I_p , E_p and an_a obtained from the analysis of forward anodic peak at scan rate of 50 mV sec^{-1} . The comparison of the data in Table-3 shows that the heterogeneous rate constant for the electro-oxidation of methanol is higher on 10 % Pt-catalyst as compared with smooth Pt-strip electrode.

Table-3: Kinetic data for electro-oxidation of 0.2 M CH_3OH on smooth Pt-strip and 10 % Pt-catalyst in 0.5 M H_2SO_4 solution at scan rate of 50 mV sec^{-1} .

Type of catalyst	Peak current (mA)	Peak potential (V)	$k_s \times 10^{-5}$ at 0.7 V (cm sec^{-1})
Smooth Pt-strip	2.90	0.86	0.36
10 % Pt-catalyst	5.51	0.93	3.09

Thermodynamic Studies

Different thermodynamic parameters were evaluated by using eq. 9 proposed by Marcus [28], which can be expressed in a simpler form for one mole of a reacting species as [12, 26, 27]:

$$k_s = Z_{\text{het}} \exp\left[\frac{-\Delta G^*}{RT}\right] \quad (9)$$

where ΔG^* is the free energy of activation and Z_{het} is the collision number for heterogeneous electron transfer process and its value can be calculated at given temperature from the following relation [28]:

$$Z_{\text{het}} = \left(\frac{RT}{2\pi M}\right)^{1/2} \quad (10)$$

where M is the molecular mass of the reacting species (methanol in this case) and other terms have their usual meanings. On rearranging eq. 9, we get

$$\ln\left(\frac{k_s}{Z_{\text{het}}}\right) = \frac{-\Delta G^*}{RT} \quad (11)$$

$$\text{Since } \Delta G^* = \Delta H^* - T\Delta S^* \quad (12)$$

Therefore, the eq. 11 can be re-written as

$$\ln\left(\frac{k_s}{Z_{\text{het}}}\right) = \frac{-\Delta H^*}{RT} + \frac{\Delta S^*}{R} \quad (13)$$

The values of k_s for electro-oxidation of 0.2 M CH_3OH were evaluated at scan rate of 50 mV sec^{-1} at different temperatures and the corresponding plots of $\ln(k_s/Z_{\text{het}})$ vs. $1/T$ for 10 % Pt-catalyst and smooth Pt-strip are shown in Fig. 6. The values of ΔH^* and ΔS^* were obtained from the slope and intercept of the plot of $\ln(k_s/Z_{\text{het}})$ 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 eqn. 12 and are given in Table-4. The values of ΔG_{298}^* were positive which indicates that the process of electro-oxidation of methanol on fuel cell catalysts is an endothermic and non-spontaneous.

The comparison of the thermodynamic data in Table-4 shows that the value of ΔH^* is more

Table-4: Thermodynamic data for electro-oxidation of methanol on smooth Pt-strip and 10 % Pt-catalyst.

Type of catalyst	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ K ⁻¹	ΔG^\ddagger kJ mol ⁻¹	Regression coefficient "R ² "
Smooth Pt-strip	57	74	35	0.98
10 % Pt-catalyst	26	-10	29	0.99

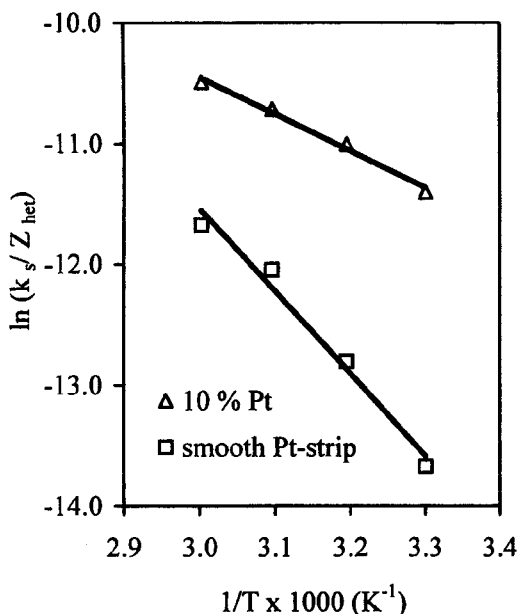


Fig. 6: Plots of $\ln(k_s / Z_{het})$ against $1/T$ for electro-oxidation of 0.2 M CH_3OH in 0.5 M H_2SO_4 on smooth Pt-strip and 10 % Pt-catalyst.

positive for electro-oxidation of methanol on smooth Pt-strip as compared to that on 10 % Pt-catalyst. It means that the electro-oxidation of methanol is less favorable on smooth Pt-strip and more favorable on carbon supported 10 % Pt-catalyst.

Experimental

Chemicals and Apparatus

All the chemicals were of analytical grades obtained from Merck (Germany). All solutions were prepared in deionized water. The electrochemical cell consisted of platinum working electrode, platinum gauze as counter electrode and Ag/AgCl (sat. KCl) as reference electrode. A model 173 potentiostat/galvanostat equipped with model 179 digital coulometer, model 175 universal programmer and model 178 electrometer probe, all from EG&G Princeton Applied Research (PAR), New Jersey,

USA, were used for cyclic voltammetric measurements. The cyclic voltammograms were recorded with model RE 0089 X-Y recorder from Houston Instruments. 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.

The electrochemical cell was placed in thermostat water bath for controlling the temperature of the working solutions. All experiments were carried out at 25°C except when measuring the thermodynamic parameters. Before each measurement, the working solution was purged with nitrogen gas.

Preparation of Working Electrodes

The electrode consisting of smooth Pt-strip was fabricated by spot welding a smooth Pt-strip onto the end of a short length of Pt-wire sealed in Pyrex glass tube. The total geometric surface area of the smooth Pt-strip electrode that may come in direct contact with the working solution was 3.04 cm². The working electrode of 10 % Pt-catalyst supported on Vulcan XC-72 was also prepared for electrochemical study. Since there are wide varieties of well-developed methods for preparation catalysts [4, 13, 29-31]; therefore, the commercial catalyst containing 10 % Pt supported on Vulcan XC-72 obtained from ElectroChem Inc., was used for cyclic voltammetric measurements.

The carbon-supported catalyst was coated onto the surface of graphite rod ($\varnothing = 1.0$ cm) for electrochemical measurements. The graphite rod was insulated from the sides by using epoxy resin. The 8 mg mL⁻¹ suspension of carbon-supported catalyst was prepared in deionized water by ultrasonic mixing. The 30 μL of the suspension was pipetted 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.

Conclusions

The comparative study of electro-oxidation of methanol on smooth Pt-strip and 10 % Pt-catalyst supported on Vulcan XC-72 was made in acidic medium using cyclic voltammetry. The electro-oxidation of methanol was found to be an irreversible

process giving only anodic peaks in both anodic and cathodic sweeps. The comparison of the catalytic activities of smooth Pt-strip and 10 % Pt-catalyst was made by evaluation of real surface area, exchange current densities, peak current and heterogeneous rate constants. The thermodynamic parameters have also been evaluated from the analysis of heterogeneous rate constants obtained at different temperatures. The kinetic and thermodynamic data showed that the electro-oxidation of methanol is less favorable on smooth Pt-strip and more favorable on 10 % Pt-catalyst supported on Vulcan XC-72.

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