

Comparison of Catalytic Activities of Carbon Supported Pt and Pt-Ru Catalysts for Methanol Oxidation in Neutral and Basic Media by Cyclic Voltammetry

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The catalytic activities of an equal amount of 3 different carbon supported catalysts containing 10% Pt, 20% Pt + 10% Ru, and 30% Pt were evaluated in neutral and basic media for methanol oxidation by cyclic voltammetry. The prominent oxidation peak for methanol appeared in the forward anodic sweep at around 1.0 V in neutral medium, while in basic medium it appeared at significantly lower potential close to 0.2 V. The peak current for methanol oxidation was higher on a catalyst containing higher Pt loading. The comparison of polarization behavior of 20% Pt + 10% Ru and 30% Pt catalysts showed that the presence of Ru increases the catalytic activity at the lower polarization region. The enhancement of catalytic activity by Ru was more obvious in basic medium as compared with neutral medium. The heterogeneous rate constants were evaluated from peak current data. At room temperature, the heterogeneous rate constant for methanol oxidation on a given catalyst was higher in basic medium as compared with neutral medium. The effect of temperature on peak current was investigated. At lower temperature, the catalytic activities were lower in neutral medium but approached near that in basic medium at higher temperature owing to the higher apparent enthalpy of activation " ΔH^* " for methanol oxidation in neutral medium. The ΔH^* values were calculated from the analysis of peak current data and found to be in the range 24 to 27 kJ mol⁻¹ in neutral medium and 15 to 17 kJ mol⁻¹ in basic medium.

Key Words: Cyclic voltammetry, methanol, neutral and basic media, fuel cell catalysts, kinetics, enthalpy of activation.

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Introduction

Fuel cells are electrochemical energy conversion devices in which the fuel (e.g., hydrogen and methanol) is supplied continuously to the anode, where it is oxidized to release electrons, which are transferred to the cathode side through an external circuit, reducing the oxidant species (usually oxygen).¹ The efficiency of energy conversion in fuel cells is dependent on the catalytic activities of the catalyst materials used at the electrode. Pt and Pt-Ru are the most efficient and stable catalysts for triggering electrochemical reactions in low temperature fuel cells.²⁻⁴ Different bimetallic catalysts containing noble and non-noble metals are being studied with different preparation methods for cost reduction and enhancement of catalytic activities of the catalysts.⁵⁻¹¹ The catalytic activities of catalysts are best assessed by electrochemical methods by finding the kinetic parameters for a certain desired electrochemical reaction, e.g., oxygen reduction and methanol oxidation.⁵⁻¹²

Cyclic voltammetry is a well-developed electrochemical technique for the kinetic study of electron transfer processes.¹³⁻¹⁵ Methods developed by Klinger and Kochi¹⁴ and Nicholson and Shain¹⁵ can be used for the determination of heterogeneous rate constants. Cyclic voltammetry has also been used for characterization of platinum based catalysts for methanol oxidation.^{12,16-21}

In the present study, cyclic voltammetric studies in neutral and basic media were conducted on 3 different carbon supported fuel cell catalysts containing 10% Pt, 20% Pt + 10% Ru, and 30% Pt for comparison of their catalytic activities for methanol oxidation. The catalytic activities of an equal quantity of each catalyst for methanol oxidation were compared, irrespective of the amount of precious metal present in the bulk catalyst material, for better comparison of the effect of a given Pt loading on the performance of a given catalyst in a given electrolytic medium. The catalytic activities were evaluated from the peak current data and polarization curves. The Nicholson and Shain¹⁵ approach was utilized for evaluation of rate constants from peak current data. The effect of temperature on the methanol oxidation peak current was also studied and the values of enthalpy of activation " ΔH^* " were evaluated from the analysis of peak current data.

Experimental

Equipment and Chemicals

A model 173 Potentiostat/Galvanostat, 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. All chemicals were analytical grade. All solutions were prepared in deionized water. Before each measurement, the working solution was purged with nitrogen gas. The electrochemical cell was placed in a 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.

Nature of Cell

The electrochemical cell consisted of platinum catalysts as working electrodes, platinum wire gauze as counter electrode, and Ag/AgCl (sat. KCl) as reference electrode. As it is customary to quote the electrode potential

with respect to the reversible hydrogen electrode (RHE) for quick reference, all potentials throughout this paper are also reported against RHE.

Preparation of working electrodes

Working electrodes were prepared using 3 different catalysts containing 10% Pt, 20% Pt + 10% Ru, and 30% Pt, all supported on Vulcan XC-72 carbon. The catalyst may be prepared by using wide varieties of methods.^{8,9,20,22} In the present study, the commercial catalysts were used to find different characteristics of methanol oxidation and to compare the catalytic activities of catalysts having different active Pt metal loadings. The catalysts were pasted onto the surface of a graphite rod ($\varnothing = 1.0$ cm), which was insulated from the sides using epoxy resin. A 8.0 mg mL^{-1} suspension of a given catalyst was prepared in deionized water by ultrasonic mixing and then $30 \mu\text{L}$ of the suspension was pipetted out and spread over the graphite surface followed by application of $20 \mu\text{L}$ of Nafion solution (5 wt. %) and drying at 30°C . Since an equal quantity of the 10% Pt, 20% Pt + 10% Ru, and 30% Pt catalyst was utilized in making working electrodes, the amount of active Pt metal in each working electrode may be calculated to be 24, 48, and $72 \mu\text{g}$, respectively.

Results and Discussion

Cyclic Voltammetric Characteristics in Neutral Medium

The cyclic voltammograms for electro-oxidation of methanol in 0.5 M NaClO_4 on different platinum catalysts are shown in Figure 1. The oxidation of methanol gives only anodic peaks in both anodic and cathodic sweeps. The anodic peak for methanol oxidation obtained in the forward anodic sweep is indicated as A, while the anodic peak obtained in the reverse cathodic sweep is indicated as B. Peak B is smaller than peak A. At the more cathodic potential side, an additional reduction peak appeared, which has been reported to arise by the reduction of hydrogen ions produced during the electro-oxidation of methanol.¹²

Cyclic Voltammetric Characteristics in Basic Medium

In this case methanol oxidation also gives only anodic peaks in both anodic and cathodic sweeps, which are indicated as A and B in the same way as in neutral medium. The forward anodic peak A appeared at around 0.20 V as shown in Figure 2. After peak formation, the anodic current dropped and remained low until the evolution of oxygen began above 0.7 V . In the cathodic sweep, the oxidation of methanol recommenced below 0.0 V and gave a small reverse anodic peak B.

Comparison of Cyclic Voltammetric Characteristics in Neutral and Basic Media

The cyclic voltammetric parameters were evaluated from the analysis of the forward anodic peak in both neutral and basic media because the forward anodic peak was not dependent on the anodic potential limit, while the reverse anodic peak was dependent on the anodic potential limit particularly because of the formation of oxides on the surface of the electrode, which caused the shift of the reverse anodic peak toward the cathodic potential side. The comparison of the forward anodic peak current and peak potential of methanol oxidation on different catalysts is given in Table 1. The data show that on a given catalyst the

peak current is higher in basic medium as compared with neutral medium. It is also apparent from Table 1 that the 30% Pt catalyst gives the highest peak current in both neutral and basic media.

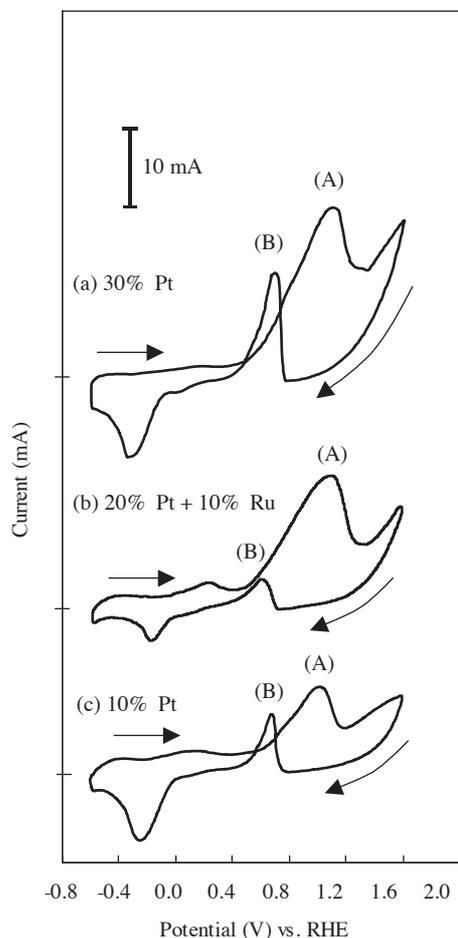


Figure 1. Cyclic voltammograms in 0.5 M NaClO₄ + 0.2 M CH₃OH at 50 mV s⁻¹ scan rate (a) 30% Pt catalyst, (b) 20% Pt + 10% Ru catalyst, (c) 10% Pt catalyst.

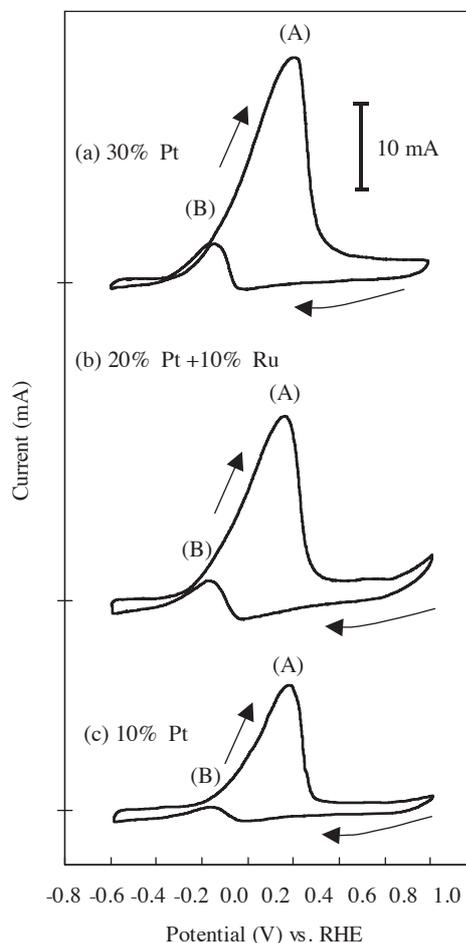
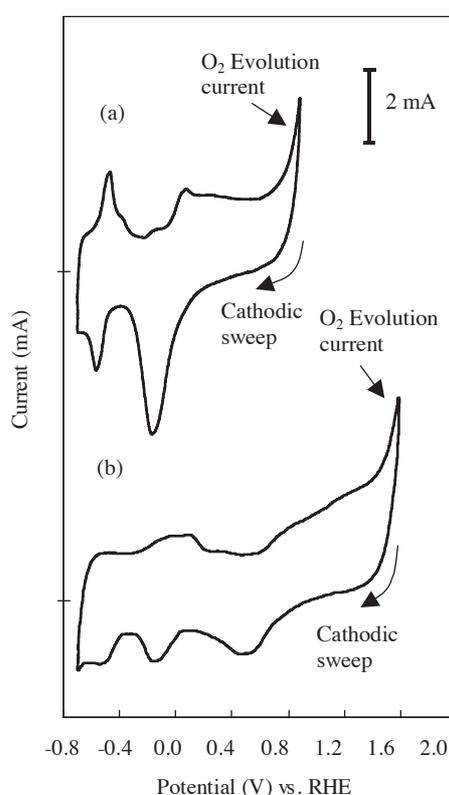


Figure 2. Cyclic voltammograms in 0.5 M KOH + 0.2 M CH₃OH at 50 mV s⁻¹ scan rate (a) 30% Pt catalyst, (b) 20% Pt + 10% Ru catalyst, (c) 10% Pt catalyst.

The peak potentials are significantly different in neutral and basic media. This difference in peak potential may be interpreted on the basis of the fact that electro-oxidation of methanol occurs via adsorption on free sites of the platinum electrode, which are not covered with adsorbed hydrogen or oxides/hydrous oxides.¹² The onset potential for the formation of oxides/hydrous oxide and subsequent evolution of O₂ are significantly different in neutral and basic media. For convenience, the comparison of cyclic voltammograms of 30% Pt catalyst in blank neutral and basic media is given in Figure 3. It is obvious from Figure 3(a) that in basic medium the electrode surface becomes covered with oxide/hydrous oxides at above 0.0 V and the oxygen evolution current appears above 0.7 V. On the other hand, in neutral medium the oxide formation begins at around 0.7 V and the oxygen evolution current appears above 1.5 V. This means that the oxide free surfaces of the platinum electrode for methanol oxidation are available at different potential ranges in neutral and basic media and hence the anodic peak for methanol oxidation appears at different potentials.

Table 1. The peak current and peak potential data for oxidation of 0.2 M CH₃OH in 0.5 M NaClO₄ and 0.5 M KOH at 50 mV s⁻¹ scan rate on different carbon supported catalysts.

Type of catalysts	Neutral medium		Basic medium	
	Peak potential “ E_p ” (V)	Peak current “ I_p ” (mA)	Peak potential “ E_p ” (V)	Peak current “ I_p ” (mA)
10% Pt	1.02	9.4	0.15	14.5
20% Pt + 10% Ru	1.09	15.9	0.15	21.6
30% Pt	1.11	21.5	0.20	26.0

**Figure 3.** Cyclic voltammograms in the absence of methanol at 50 mV s⁻¹ scan rate on 30% Pt catalyst (a) in 0.5 M KOH, (b) in 0.5 M NaClO₄.

Polarization Measurements

Polarization curves are drawn by plotting electrode potential “ E ” versus the logarithm of current density “ $\log i$ ”. A more catalytically active catalyst is identified from the polarization curves by using the fact that it gives the highest current density at any given potential and the lowest Tafel slope for a given electrochemical reaction.

The polarization curves for methanol oxidation on different catalysts in neutral and basic media are shown in Figure 4(a) and (b). The current-potential data were obtained from the analysis of the rising

portion of the forward anodic peak. The comparison of the polarization curves shows that the 30% Pt catalyst is more catalytically active in both neutral and basic media.

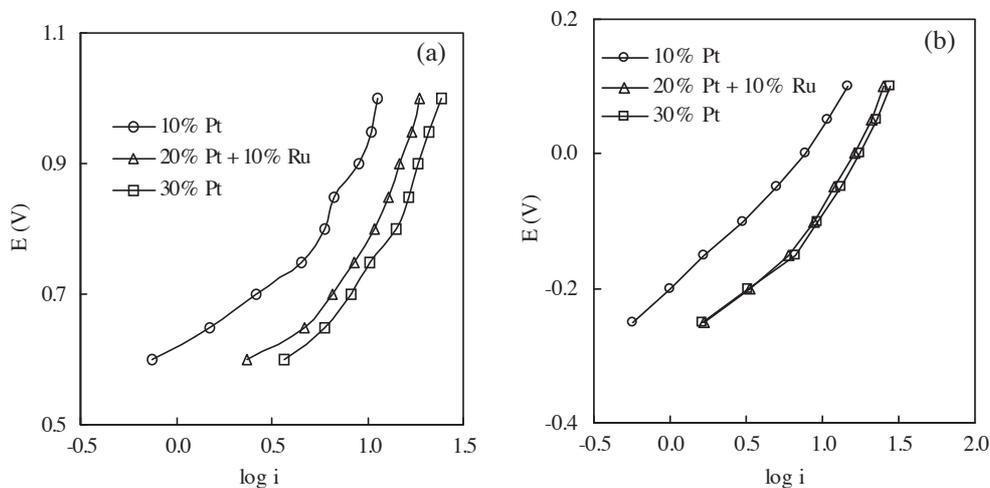


Figure 4. Polarization curves for oxidation of 0.2 M CH₃OH on different catalysts in (a) in 0.5 M NaClO₄, (b) in 0.5 M KOH.

The comparison of the lower polarization region of the 20% Pt + 10% Ru and 30% Pt catalyst also indicates the enhancement of the catalytic activity of the carbon supported Pt catalysts by the Ru atoms, which is more prominent in basic medium as compared with neutral medium. In basic medium the catalytic activity of the 20% Pt + 10% Ru catalyst is almost the same as that of the 30% Pt catalyst at the lower polarization region. The greater enhancement of the catalytic activity of the carbon supported Pt-catalyst by Ru atoms in basic medium may be attributed to the effective formation of hydrous oxides on the carbon supported Ru atoms at the lower polarization region. These adsorbed hydrous oxides may contribute to the overall rate of methanol oxidation via their participation in the removal of the adsorbed CO, the so-called bi-functional mechanism.⁴

The kinetic parameters may be evaluated from polarization curves using the following equation:^{12,13}

$$E = E^o - b \log i^o + b \log i \quad (1)$$

where b is the Tafel slope and i^o is the exchange current density at reference potential " E^o ", which is known as the equilibrium potential or standard electrode potential.

The values of the Tafel slope were evaluated by finding the slope of plot E vs. $\log i$ at the lower polarization region. The comparison of the polarization data in Tables 2 and 3 indicates that the values of the Tafel slope are slightly higher in neutral medium as compared with basic medium. The values of product of electron transfer coefficient and number of electrons involved in the rate-determining step " αn_a " were calculated from the values of Tafel slopes.^{12,13} If one assume $\alpha = 0.5$, then the number of electrons in the rate-determining step may be calculated to be in the range 0.3 to 0.6. It indicates the complex nature of the methanol oxidation reaction involving the formation of strongly bound CO that may passivate the electrode surface during continuous runs. It also indicates that there may not be more than one electron involved in the rate-determining step.

Table 2. Polarization data for oxidation of 0.2 M CH₃OH in 0.5 M NaClO₄.

Type of catalysts	Intercept of E vs. $\log i$	Tafel slope "b" (V decade ⁻¹)	αn_a	i^o (mA cm ⁻²) at 0.0 V
10% Pt	0.618	0.215	0.279	0.001
20% Pt + 10% Ru	0.474	0.294	0.204	0.024
30% Pt	0.390	0.351	0.171	0.077

Table 3. Polarization data for oxidation of 0.2 M CH₃OH in 0.5 M KOH.

Type of catalysts	Intercept of E vs. $\log i$	Tafel slope "b" (V decade ⁻¹)	αn_a	i^o (mA cm ⁻²) at 0.0 V
10% Pt	-0.199	0.211	0.284	8.77
20% Pt + 10% Ru	-0.312	0.228	0.263	23.36
30% Pt	-0.306	0.215	0.279	26.50

The intercept of the plot of E vs. $\log i$ may give the value of exchange current density " i^o " provided the standard electrode potential " E^o " is known for methanol oxidation in given electrolytic media (neutral and basic in this case). Since the oxidation of methanol is an irreversible process giving only anodic peaks in both anodic and cathodic sweeps, the evaluation of E^o from cyclic voltammetric data is difficult. Moreover, the oxidation of methanol occurs at different potential ranges in neutral and basic media; therefore, the evaluation of i^o at a certain potential other than E^o may not give a good comparison of the catalytic activity of a given catalyst in different electrolytic media.

It has been reported that if the intercept of the plot of E vs. $\log i$ is known then one can evaluate the approximate value of i^o at any desired potential from the values of the Tafel slope and the intercept.¹² In the present work, the values of i^o at 0.0 V were calculated in both neutral and basic media from the analysis of the lower polarization data of the intercept and Tafel slope. It is obvious from the polarization data in Tables 2 and 3 that exchange current density increases with increasing Pt loading.

Evaluation of Heterogeneous Rate Constant from Peak Current Data

The rate of an electrochemical process may be calculated using different approaches, e.g., Klinger and Kochi,¹⁴ and Nicholson and Shain.¹⁵ The oxidation of methanol on platinum seems difficult to fit into these expressions because it is a multistep process in which dehydrogenation steps along with charge transfer take place until strongly bound CO-like intermediates are formed, which are removed during interaction with adsorbed hydrous oxides.¹² Since all intermediate steps during methanol oxidation are assumed to be fast steps (except for the removal of CO), the rate of overall methanol oxidation may be assumed to be controlled by the oxidation of adsorbed CO, which may occur as follows:^{12,19}



The approximate values of heterogeneous rate constants for the oxidation of methanol on smooth Pt foil at 0.7 V have been reported in acidic and neutral media.¹² Since in the present case the peak potentials are

different in neutral and basic media, the Nicholson and Shain¹⁵ approaches were utilized to evaluate the heterogeneous rate constants at peak potential. It is generally agreed that the rate constant at any potential “ E ” is given by the following relation:^{13–15}

$$k(E) = k_s \exp \left[\frac{\alpha n_a F}{RT} (E - E^o) \right] \quad (3)$$

where E is the electrode potential, αn_a is the product of electron transfer coefficient and the number of electrons transferred in the rate determining step, and E^o is the standard electrode potential that fixes the value of k_s (i.e. k_s is the value of the heterogeneous rate constant at E^o). The other factors have their usual meanings.

Nicholson and Shain¹⁵ solved this equation and obtained a simple relation between peak current and heterogeneous rate constant for a totally irreversible electron transfer process, which for an anodic process may be given as

$$I_p = 0.227 n F A C k_s \exp \left[\frac{\alpha n_a F}{RT} (E_p - E^o) \right] \quad (4)$$

where I_p is the peak current (in amperes), n is the total number of electrons transferred in the overall reaction (in this case 6), 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 rearrangement of Eq. (3), we get

$$\frac{I_p}{0.227 n F A C} = k_s \exp \left[\frac{\alpha n_a F}{RT} (E_p - E^o) \right] \quad (5)$$

Comparison of Eqs. (3) and (5) indicates that the heterogeneous rate constant at peak potential may be given as

$$k(E_p) = \frac{I_p}{0.227 n F A C} \quad (6)$$

According to this equation, the rate constant at peak potential $k(E_p)$ needs only the data of peak current for oxidation of a given concentration of methanol. The calculated values of $k(E_p)$ in basic and neutral media at 25 °C are presented in Table 4. The comparison of the data shows that the rate of oxidation of methanol is the highest on 30% Pt catalyst in both neutral and basic media as compared with the other 2 catalysts. The data also show that the rate of electro-oxidation of methanol on a given catalyst is higher in basic medium as compared with neutral medium.

Effect of Temperature on the Peak Current

The peak current of electro-oxidation of methanol increases with increasing temperature. The effect of temperature on peak current is more significant in neutral medium as compared with basic medium and hence at higher temperature the apparent peak current in neutral medium becomes close to that in basic medium as shown by the data in Table 5. This observation may be interpreted in terms of higher enthalpy of activation for oxidation of methanol on carbon-supported catalysts in neutral medium due to which the catalytic activity increases significantly with the rise of temperature.

Table 4. Heterogeneous rate constants at peak potential for oxidation of 0.2 M CH₃OH in 0.5 M NaClO₄ and 0.5 M KOH on different carbon supported catalysts at 50 mV s⁻¹ cscan rate and 25 °C.

Type of catalysts	$k(E_p) \times 10^{-4}$ (cm s ⁻¹)	
	Neutral medium	Basic medium
10% Pt	1.03 ± 0.03	1.57 ± 0.05
20% Pt + 10% Ru	1.73 ± 0.04	2.38 ± 0.04
30% Pt	2.30 ± 0.06	2.89 ± 0.05

Table 5. Comparison of peak current data for methanol oxidation on different carbon supported catalysts in 0.5 M NaClO₄ and 0.5 M KOH at different temperatures.

Temp. (K)	I_p (mA)					
	Neutral medium			Basic medium		
	10% Pt	20% Pt + 10% Ru	30% Pt	10% Pt	20% Pt + 10% Ru	30% Pt
303	10.2	18.1	24.4	16.5	23.6	29.3
313	15.0	26.0	34.8	18.9	29.1	33.8
323	20.1	35.4	46.2	23.6	35.4	42.8
333	27.3	44.5	58.8	30.0	41.7	50.6

The apparent values of enthalpy of activation “ ΔH^* ” for a given electrochemical reaction at a given concentration may be evaluated from peak current data using the following relation:^{16,23}

$$\frac{\delta \ln I_p}{\delta(1/T)} = \frac{\Delta H^*}{R} \quad (7)$$

i.e. the slope of plot of logarithm of peak current “ $\ln I_p$ ” versus $1/T$ is equal to $\Delta H^*/R$, where R is the gas constant taken as 8.3143 J K⁻¹ mol⁻¹.

The values of ΔH^* for methanol oxidation on different carbon supported catalysts were evaluated from the slope of $\ln I_p$ versus $1/T$ (Figure 5) and are compared in Table 6. In all cases, the values of ΔH^* are positive, which indicates that oxidation of methanol on carbon supported platinum catalysts is an activation controlled process. The values of ΔH^* obtained on all carbon supported catalysts with different active metal (Pt) loadings are in the same range in neutral medium as well as in basic medium. However, the ΔH^* values are significantly higher in neutral medium as compared with basic medium. Due to this higher value of ΔH^* , the peak current increases significantly with the rise in temperature in neutral medium as compared with basic medium.

Table 6. Apparent heat of activation data of methanol oxidation on different carbon supported catalysts in 0.5 M NaClO₄ and 0.5 M KOH.

Type of catalysts	ΔH^* kJ mol ⁻¹	
	Neutral Medium	Basic Medium
10% Pt	27.2 ± 0.1	16.7 ± 0.4
20% Pt + 10% Ru	24.9 ± 0.4	16.1 ± 0.3
30% Pt	24.5 ± 0.2	16.0 ± 0.2

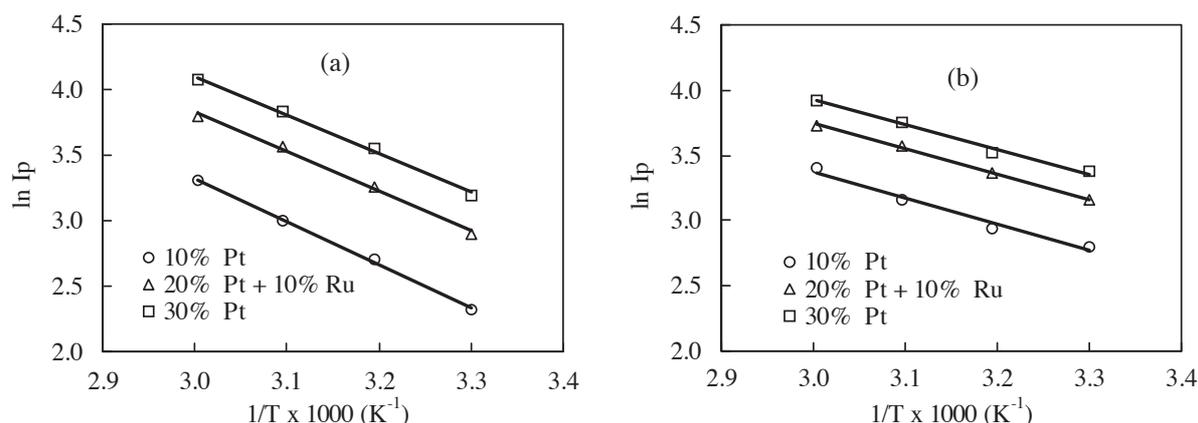


Figure 5. Plot of $\ln I_p$ vs. $1/T$ in neutral and basic media (a) in 0.5 M NaClO_4 , (b) in 0.5 M KOH .

Conclusions

The cyclic voltammetric studies in neutral and basic media were done on 3 different carbon supported fuel cell catalysts containing 10% Pt, 20% Pt + 10% Ru, and 30% Pt for comparison of their catalytic activities for methanol oxidation. The catalytic activities were higher on those catalysts containing higher Pt loading. The presence of Ru with Pt was found to increase the catalytic activity at the lower polarization region. The enhancement of the catalytic activity of carbon supported Pt-catalyst by Ru atoms was more prominent in basic medium and it was attributed to the effective formation of hydrous oxides on Ru atoms that may contribute to the overall methanol oxidation via their participation in the removal of adsorbed CO. The heterogeneous rate constants at peak potential " k (E_p)" were evaluated and discussed for comparison of catalytic activity of different catalysts. At lower temperature, the catalytic activities were lower in neutral medium but approached those in basic medium at higher temperature owing to the higher enthalpy of activation " ΔH^* " for methanol oxidation in neutral medium. The ΔH^* values were calculated from the analysis of peak current data and found to be in the range 24 to 27 kJ mol^{-1} in neutral medium and 15 to 17 kJ mol^{-1} in basic medium.

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