



CYCLIC VOLTAMMETRIC STUDY OF ELECTRO-OXIDATION OF METHANOL ON PLATINUM ELECTRODE IN ACIDIC AND NEUTRAL MEDIA

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The electro-oxidation of methanol on electrochemically treated platinum foil was investigated in acidic and neutral media for comparison of cyclic voltammetric characteristics and elucidation of mechanism of electro-oxidation of methanol. The surface area and roughness factor of platinum electrode was calculated. The electro-oxidation of methanol is an irreversible process giving anodic peaks in both anodic and cathodic sweep. The characteristic peaks of electro-oxidation of methanol appeared at almost the same potential region in both acidic and neutral media. In neutral medium, certain additional cathodic/anodic peaks appeared which were confirmed to arise by the reduction/oxidation of hydrogen ions. The exchange current density and heterogeneous electron transfer rate constant was higher in neutral medium as compared with acidic medium. The thermodynamic parameters ΔH^\ddagger , ΔS^\ddagger , and ΔG_{298}^\ddagger were calculated. The values of ΔH^\ddagger and ΔG_{298}^\ddagger were positive which indicated that the process of electro-oxidation of methanol is an endothermic and non-spontaneous. The mechanism of electro-oxidation of methanol was same in both acidic and neutral media involving the formation of various adsorbed intermediate species through dissociative adsorption steps leading to the formation of CO adsorbed radicals, which are removed during interaction with adsorbed hydrous oxides provided by the oxidation of adsorbed water molecules. The higher rate of electro-oxidation of methanol in neutral medium was interpreted in the light of electrochemical mechanism and was attributed to the presence of comparatively small amount of hydrogen ions only along the surface of working electrode, which are produced during electro-oxidation of methanol.

Keywords: Methanol, Cyclic voltammetry, Acidic & neutral medium, Thermodynamic, Mechanism, Hydrous oxide

1. Introduction

The electro-oxidation of methanol has been extensively studied since 1960's mainly due to its possible use as liquid fuel in fuel cells [1-3]. Most of the authors have studied the electro-oxidation of methanol in acidic environment for finding the catalytic activity of different catalysts [4-6]. The complete electro-oxidation of methanol to CO₂ yields six electrons per molecule and it involves an oxygen insertion process. This oxygen cannot be supplied directly by adsorbed water molecules because the effective electrochemical decomposition of water molecules does not commence before the potential exceeds 0.85 V [7]. On the basis of radiometric method of determination of adsorption of methanol using tritium labeled at methyl group, it has been found that CH₃OH adsorption involves homolytic rupture of C-H bond that leads to the formation of Pt-C bond [8]. During methanol electro-oxidation the electrode surface is progressively blocked by the formation of inactive adsorbed intermediate species e.g. (C \ddot{O})_{ad} [9, 10] and (C $\ddot{O}H$)_{ad} [11, 12]. The (C $\ddot{O}H$)_{ad} radical occupies three sites while (C \ddot{O})_{ad} radical occupies two sites on the surface

of platinum electrode. The formation of these inactive adsorbed intermediate species deactivates the Pt-surface for further electro-oxidation of methanol.

Cyclic voltammetry is a well-established technique for the study of kinetics and mechanism of electron transfer processes [13-16] and in the present work it has been used to investigate the electro-oxidation of methanol on platinum electrode in acidic and neutral media. Surface area, exchange current densities, rate constants and thermodynamic parameters were calculated. Various results were discussed for elucidation of mechanism of electro-oxidation of methanol on platinum electrode.

2. Experimental

2.1 Equipments 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 of analytical grade. The solutions were prepared in deionized water. A 50

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ml working solution was analyzed in an electrochemical cell each time. The working solution was deoxygenated by nitrogen bubbling.

2.2. Nature of electrochemical cell

A glass beaker-type electrochemical cell equipped with a 3.04-cm² smooth platinum foil spot-welded onto a short length of Pt-wire as working electrode, large surface area platinum wire gauze as counter electrode and Ag/AgCl (sat. KCl) as reference electrode was used for all electrochemical measurements. As it is customary to quote the electrode potential with respect to the reversible hydrogen electrode "RHE" for quick reference, therefore, all potentials throughout this paper are also referred to RHE.

2.3 Treatment of working electrode

The Pt-electrode was cleaned by treating it with a freshly prepared 1:1 mixture of conc. H₂SO₄ and HNO₃ for 30 seconds followed by thorough rinsing with deionized water. It was then electrochemically activated in 0.5 M H₂SO₄ by holding the electrode for one minute at an anodic potential of 1.8 V to remove any inactive adsorbed species formed during oxidation process. The electrode potential was then lowered and held for three minutes at -0.05 V to allow the reduction of oxides layers, which are electrochemically produced at higher anodic potential. Finally the electrode was cycled between -0.05 V and 1.8 V at 500 mV sec⁻¹ scan rate for five to ten cycles and then the cleanliness of the electrode was checked by recording the cyclic voltammogram in deoxygenated 0.5 M H₂SO₄ at scan rate of 50 mV sec⁻¹ in the potential range 0.05 to 1.6 V vs. RHE. The establishment of characteristic features of Pt-electrode in acid medium as shown in Fig.1a confirmed its cleanliness.

3. Results and Discussion

3.1 Surface area and roughness factor measurement

The evaluation of real surface area and roughness factor of platinum electrode is a useful tool for comparison of the catalytic activities of different platinum catalysts. The catalytic activity of the platinum catalysts increases with increasing roughness factor. The roughness factor may be increased significantly by deposition of a few milligrams of platinum particles on high surface area carbon support [17-18].

The real surface of the Pt-electrode can be measured from its cyclic voltammogram in 0.5 M H₂SO₄ by determining the charge transferred

during the adsorption of hydrogen ions which may occur in the cathodic sweep in the potential range from 0.4 up to 0.05 V as shown in Fig. 1a along with background correction. The real surface area "S_{Pt-H}" and roughness factor "R.F" are calculated by using the following relations [18-20]:

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

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

where "Q_{Pt-H}" is the hydrogen adsorption charge and the 210 μC is a generally accepted value for the charge transferred per cm² for monolayer hydrogen adsorption (Pt: H =1: 1) on an "ideal surface" of polycrystalline platinum electrode having a roughness factor of one. The real surface area of Pt-foil was calculated to be 7.05 cm² that correspond to a roughness factor of 2.32.

3.2 Cyclic voltammetric behavior of platinum electrode in acidic medium

The cyclic voltammogram of Pt-electrode in blank acidic medium shown in Fig.1a indicates the same characteristic features as described elsewhere [21]. The process of hydrogen adsorption/desorption occurs in the potential ranges from 0.40 to 0.05V. Below 0.05 V, the current for direct evolution of hydrogen is observed due to the direct reduction of bulk hydrogen ions. Due to this hydrogen evolution reaction, the instrument may show overloading and hence the potential region below 0.05 V was avoided. The hydrogen adsorption in the cathodic sweep gives two cathodic peaks, H_{c1} and H_{c2} while the hydrogen desorption in the anodic sweep gives three anodic peaks designated as H_{A1}, H_i, H_{A2}. The intermediate peak H_i is very small. The significant formation of hydrous oxides begins above 0.80V and the surface of Pt-electrode in the potential range from 1.2 to 1.5 V is assumed to be covered with compact hydrous oxides and oxides. The current for the direct evolution of molecular oxygen is observed above 1.5 V. The hydrous oxides and oxides are reduced in the subsequent cathodic sweep and give rise to a well-defined oxide reduction peak at 0.73 V designated as O_c.

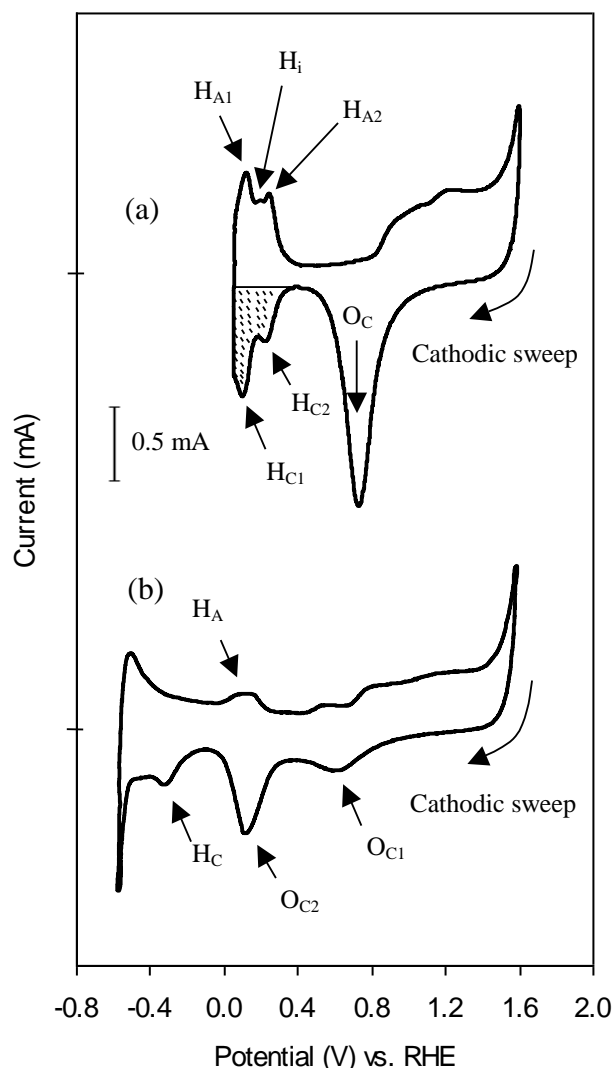


Figure 1. Comparison of the cyclic voltammetric characteristics of platinum electrode (a) Cyclic voltammogram of platinum electrode in 0.5 M H_2SO_4 in the potential range 0.05 to 1.6 V at 50 mV sec^{-1} scan rate. The shaded area in the cathodic sweep in the potential range 0.4 to 0.05 V is the hydrogen adsorption region (b) Cyclic voltammogram of platinum electrode in 0.5 M NaClO_4 in the potential range -0.60 to 1.6 V at 50 mV sec^{-1} scan rate.

3.3. Cyclic voltammetric behavior of platinum electrode in neutral medium

In neutral medium (Fig.1b) the potential range can be increased from -0.60 V to 1.6 V . The hydrogen adsorption /desorption regions are not well defined in this case. In the anodic sweep, the hydrogen desorption gives a small peak H_A at around 0.12 V . The surface of platinum electrode in the potential region above 0.80 V is almost similar to that in acidic medium and is assumed to

be covered with oxides/hydrous oxides. In the cathodic sweep, the reduction of oxides gives two cathodic peaks O_{C1} and O_{C2} at 0.61 and 0.13 V respectively. After the reduction of oxides the hydrogen adsorption occurs on the free surface of platinum electrode and gives a small peak H_c at -0.33 V . The current for direct evolution of molecular hydrogen is observed below -0.50 V .

3.4. Electro-oxidation of methanol in acidic medium

In acidic medium, the electro-oxidation of methanol gives a well-defined forward anodic peak (Peak-I) in the anodic sweep at 0.85 V along with an ill-defined shoulder at around 0.70 V . After the formation of Peak-I, the anodic current rises again and gives a broad anodic peak lying around 1.4 V i.e. just after the forward anodic peak. In the subsequent cathodic sweep, the reduction of electroadsorbed species (compact hydrous oxide and oxide) occurs and methanol electro-oxidation recommences when significant O-electroadsorbed species have been reduced. The recommencement of methanol electro-oxidation in the cathodic sweeps gives a reverse anodic peak (Peak-II) at 0.66 V . The appearance of an anodic peak in both anodic and cathodic sweep is attributed to the high catalytic activity of Pt-electrode for methanol electro-oxidation.

The characteristic hydrogen adsorption/desorption peaks of platinum electrode in acidic medium disappeared in the presence of methanol in supporting electrolyte, which may be attributed to the blocking of active sites (which are free from any adsorbed species) of platinum electrode by certain adsorbed intermediate species formed during the electro-oxidation of methanol.

3.5. Electro-oxidation of methanol in neutral medium

In neutral medium, the forward anodic peak (Peak-I) appeared at 0.85 V along with a shoulder at around 0.66 V as shown in Fig. 2a. After peak formation the anodic current rises again and gives a broad anodic peak at around 1.4 V . In the cathodic sweep, a reverse anodic peak "Peak-II" appears at 0.66 V . The reverse anodic peak is smaller than the forward anodic peak.

An additional cathodic peak "C1" is also obtained at -0.18 V in the cathodic sweep during reversal of anodic sweep at a certain potential along the way up the forward anodic peak. On continuing the cycling of electrode, the corresponding anodic peak "A1" is also observed

at -0.07 V in the subsequent anodic sweep. These additional peaks did not appear on reversing the anodic sweep at 0.40 V, which lies just before the onset potential of forward anodic peak. It means that these additional peaks arise due to the reduction/oxidation of certain intermediate species formed during the electro-oxidation of methanol. These additional peaks "C1-A1" also appeared on addition of few drops of dilute acid in neutral medium even in the absence of methanol. It provides a clue that hydrogen ions may be produced during the electro-oxidation of methanol.

3.6. Comparison of cyclic voltammetric characteristics of electro-oxidation of methanol in acidic and neutral media

In both media, the electro-oxidation of methanol gives only anodic peaks in both anodic and cathodic sweeps and the forward anodic peak has an ill-defined shoulder around 0.70 V, which may have arisen by the adsorption of methanol and its oxidation in intermediate steps. In both cases, the peak potential of the forward and reverse anodic peaks is approximately the same. In both cases, a broad anodic peak appears around 1.4 V just after the forward anodic peak. The occurrence of broad anodic peak in acidic and neutral media may be due to the reaction of certain adsorbed intermediate species with the adsorbed oxide/hydrous oxide, which are available significantly above 1.2 V.

The occurrence of almost same types of anodic peaks for methanol electro-oxidation in acidic and neutral media indicates that the mechanism of electro-oxidation of methanol may be almost same in both cases. One important clue toward the elucidation of mechanism of electro-oxidation of methanol at platinum electrode was obtained by investigating the behavior of additional peaks "C1-A1" in neutral medium, which showed that hydrogen ions are produced during the electro-oxidation of methanol.

On comparing the cyclic voltammograms of platinum electrode in the presence of methanol (Fig. 2a & 2b) with the corresponding cyclic voltammograms in the blank solution (Fig. 1a & 1b), it is found that the forward anodic peak of methanol electro-oxidation appears at the potential, which is equivalent to the onset potential of compact hydrous oxides on the platinum electrode. On the other hand the reverse anodic peak appears at the potential where significant oxide layer has been removed. It means that the electro-oxidation of methanol occurs only on the

platinum surface that is free from compact oxide/hydrous oxide. In other words, the adsorbed oxides/hydrous oxides may not be involved directly in the process of electro-oxidation of methanol. They may, however, contribute to the overall process of electro-oxidation of methanol by participating in the process of oxidation of inactive adsorbed intermediate species, which is indicated by the formation of a broad anodic peak lying just after the forward anodic peak.

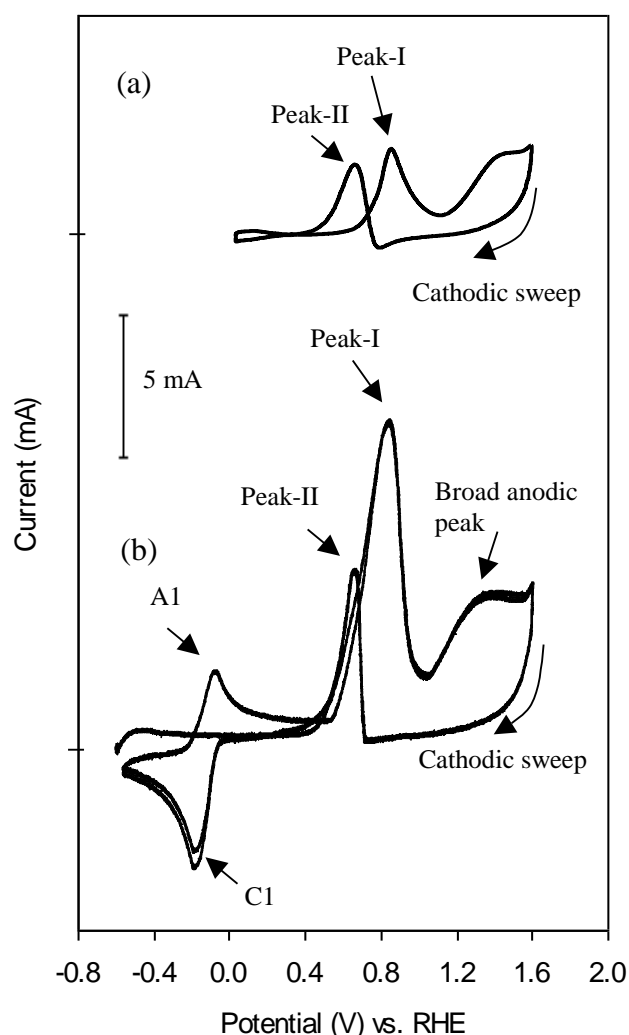


Figure 2. Comparison of the cyclic voltammetric characteristics of electro-oxidation of methanol on platinum electrode (a) 0.5 M H_2SO_4 + 0.2 M CH_3OH (b) 0.5 M NaClO_4 + 0.2 M CH_3OH . The cyclic voltammetric conditions are same as per Fig. 1.

3.7 Effect of concentration of methanol on the peak current

The peak current of the methanol electro-oxidation increases with increasing concentration

of methanol. The plot of forward anodic peak current versus the concentration of methanol in acidic and neutral media is shown in Fig.3. The comparison of the data shows that the peak current is higher in neutral medium as compared to that in acidic medium. In both cases, the peak current did not vary linearly with increasing concentration of methanol, which may be attributed to the blocking of the surface of platinum electrode with certain inactive intermediate species.

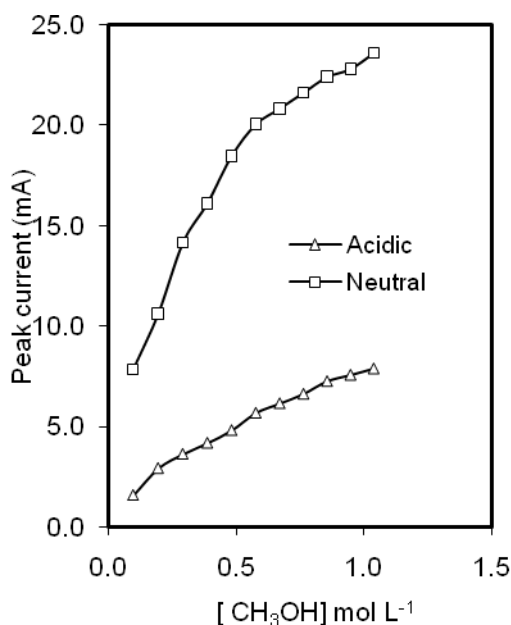


Figure 3. Comparison of the forward anodic peak current in acidic and neutral media at different concentration of methanol.

3.8 Polarization measurements

The kinetic parameters such as exchange current density and Tafel slopes were evaluated from the Tafel equation. If the ohmic drop is neglected then the Tafel equation for an anodic process can be written as [22, 23].

$$E = E_{\text{rev}} - b \log i^{\circ} + b \log i \quad (3)$$

where b is the Tafel slope (in V decade^{-1}), i is the apparent current density (in mA cm^{-2}), and i° is the exchange current density (in mA cm^{-2}) at the reversible potential " E_{rev} " of a given electrode reaction. The value of b is given by the following relation :

$$b = \frac{2.303 RT}{\alpha n_a F} \quad (4)$$

where R is the universal gas constant, T is the temperature in the Kelvin scale, F is the faraday constant, n_a is the number of electrons transferred in the rate determining step and α is the electron transfer coefficient. The value of α is equal to 0.5 for a reversible electron transfer process.

The values of current at different potentials were measured from the analysis of rising portion of forward anodic peak and then the values of potential " E " were plotted against the logarithm of the apparent current density " $\log i$ " as shown in Fig. 4. The comparison of the E vs. $\log i$ curves show that at any given value of E , the value of $\log i$ is higher for electro-oxidation of methanol in neutral medium as compared to that in acidic medium. It means that the rate of electro-oxidation of methanol is higher in neutral medium as compared to acidic medium.

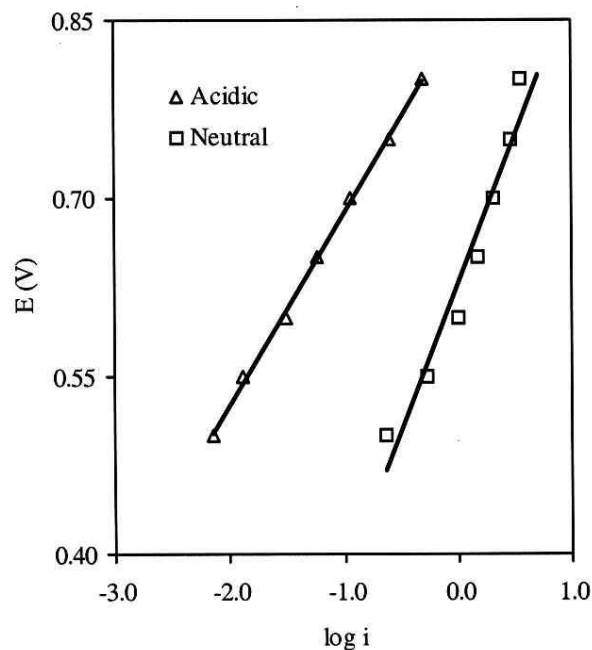


Figure 4. Plots of electrode potential " E " versus the logarithm of the apparent current density " $\log i$ " for electro-oxidation of 0.2 M CH_3OH on platinum electrode in 0.5 M H_2SO_4 and 0.5 M NaClO_4 .

The values of b , αn_a and i° evaluated from the polarization curves are given in Table 1. The exchange current densities at 0.70 V were evaluated from the intercept of the plot of E vs. $\log i$ by taking E_{rev} equal to 0.70 V just for comparison of the kinetic data at a potential of interest. This practice of comparison of kinetic data at certain potential of interest has also been used by other authors [17, 24].

The value of Tafel slope is slightly higher in neutral medium as compared to that in acidic medium but instead the current density at any potential, say 0.70 V, is higher in neutral medium. The value of αn_a is less than 0.5 in both acidic and neutral media and hence maximum of one electron may be considered to participate in the rate-determining step (i.e. the slowest step of the overall electrochemical reaction).

3.9. Evaluation of heterogeneous electron transfer rate constant

The value of heterogeneous electron transfer rate constant " k_o " may be evaluated by using the following relation for an irreversible anodic process involving n -electrons in the overall reaction [25]:

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

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), F is the faraday's constant, A is the apparent surface area of the electrode (in cm^2), C is the bulk concentration of the reactant (in mol cm^{-3}), E_p is the peak potential and E° is the standard electrode potential which fixes the value of k_o (i.e. k_o is the rate constant at E°). The other parameters have their usual meanings. The Eq. 5 can be rearranged to :

$$k_o = \frac{I_p}{0.227 n F A C} \exp\left[\frac{-\alpha n_a F}{RT} (E_p - E^\circ)\right] \quad (6)$$

The values of k_o were numerically calculated from Eq. 6 using experimental values of I_p , E_p , and αn_a . The αn_a determined from polarization measurements were utilized for evaluation of k_o . Since electro-oxidation of methanol at Pt-electrode is a totally irreversible process giving only anodic peaks in both anodic and cathodic sweeps, therefore, it is difficult to measure the standard electrode potential " E° ". For convenience the value of E° was taken 0.70 V for comparison of the rate constant at a fixed potential of interest as in case of polarization measurements [17, 24].

The comparison of the data in Table 2 shows that the value of k_o is much higher in neutral medium as compared with acidic medium. Hence, the neutral medium is more suitable for getting higher apparent current density.

3.10 Thermodynamic studies

The different thermodynamic parameters were evaluated using the relation based on Marcus theory [26], which may be expressed in simpler form for one mole of a reacting species as [16].

$$\ln\left(\frac{k_s}{Z_{\text{het}}}\right) = \frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \quad (7)$$

where Z_{het} is the collision number for heterogeneous electron transfer process and its

Table 1. Polarization data obtained from the analysis of current-potential data of the rising portion of forward anodic peak of electro-oxidation of 0.2 M CH_3OH on platinum electrode in 0.5 M H_2SO_4 and 0.5 M NaClO_4 solutions at 50 mV sec^{-1} scan rate.

Type of medium	Intercept of polarization curve	Tafel slope "b" (V decade ⁻¹)	αn_a	Exchange current density at 0.70V " $i_{(0.70 \text{ V})}^\circ$ " (mA cm^{-2})
Acidic medium	0.849	0.162	0.370	0.12
Neutral medium	0.628	0.248	0.242	1.95

Table 2. Kinetic data for electro-oxidation of 0.2 M CH_3OH on platinum electrode in 0.5M H_2SO_4 and 0.5 M NaClO_4 solutions at 50 mV sec^{-1} scan rate.

Type of medium	Peak potential " E_p " at 50 mV sec^{-1} (V)	Peak current " I_p " (mA)	$K_o \times 10^{-5}$ at 0.70 V (cm sec^{-1})
Acidic medium	0.85	2.90	0.42
Neutral medium	0.85	11.0	3.35

Table 3. Thermodynamic data for electro-oxidation of 0.2 M CH₃OH on platinum electrode in 0.5 M H₂SO₄ and 0.5 M NaClO₄ solutions.

Type of medium	ΔH^* kJ mol ⁻¹	ΔS^* J mol ⁻¹ K ⁻¹	ΔG_{298}^* kJ mol ⁻¹	Correlation coefficient "R ² "
Acidic medium	53.8	66.59	34.0	0.990
Neutral medium	23.7	-18.3	29.19	0.981

value can be calculated at any given temperature using the following relation [16]:

$$Z_{\text{het}} = \left(\frac{RT}{2\pi M} \right)^{1/2} \quad (8)$$

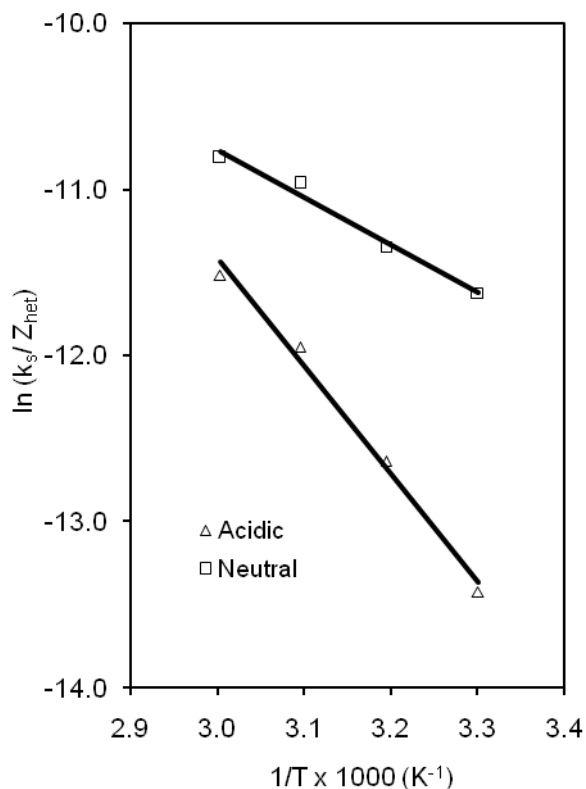


Figure 5. Arrhenius plots for electro-oxidation of methanol in 0.5 M H₂SO₄ and 0.5 M NaClO₄ on platinum electrode.

where M is the molecular mass of the reacting species.

The values of $\ln k_s/Z_{\text{het}}$ were calculated at different temperatures and were plotted against $1/T$ as shown in Fig. 5. 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 the following relation:

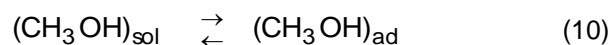
$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (9)$$

The comparison of thermodynamic data for electro-oxidation of methanol in acidic and neutral media is made in Table 3. The value of ΔH^* was positive in both cases and was higher in acidic medium as compared with neutral medium. It means that the electro-oxidation of methanol is an endothermic process and is more favorable in neutral medium. The values of ΔG_{298}^* were also positive and indicate that the process is non-spontaneous.

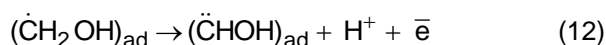
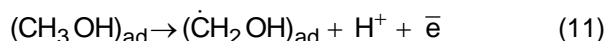
3.11 Mechanism of electro-oxidation of methanol

The electro-oxidation of methanol occurs in the potential range where the platinum surface is free from adsorbed hydrogen and oxides/hydrous oxides, which are formed during the electro-oxidation process in the specific potential range. The hydrogen ions are produced during the process of electro-oxidation of methanol as shown by the behavior of additional cathodic/anodic peaks in neutral medium. In the light of these clues, the following reaction pathways are proposed for the electro-oxidation of methanol at Pt- electrode in acidic and neutral medium:

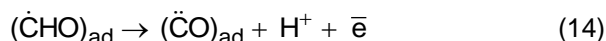
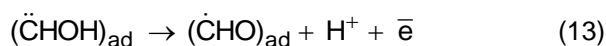
The first step of electro-oxidation of methanol is assumed to be the adsorption of methanol on the free sites of Pt- electrode [27].



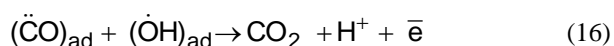
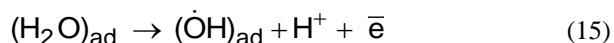
The electro-oxidation of adsorbed methanol may proceed via rupture of C-H bond of adsorbed methanol molecules that leads to the formation of different adsorbed intermediates species as described below:



Further oxidation of $(\ddot{\text{C}}\text{HOH})_{\text{ad}}$ radical may occur in two different ways i.e. either by rupture of C-H bond or O-H bond. The rupture of C-H bond may give an inactive adsorbed intermediate $(\ddot{\text{C}}\text{OH})_{\text{ad}}$ [11, 12] while the rupture of O-H bond gives active adsorbed intermediates which ultimately gives rise to the formation of $(\ddot{\text{C}}\text{O})_{\text{ad}}$ radical. Most of the authors have recognized the formation of $(\ddot{\text{C}}\text{O})_{\text{ad}}$ [9, 10, 27, 28] which may proceed as follows:

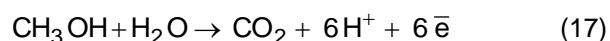


The intermediate steps 11 to 14 are considered to be fast steps involving the formation of active intermediate species and hence they don't give any well-defined anodic peaks. The overall reaction may be controlled by the oxidation of $(\ddot{\text{C}}\text{O})_{\text{ad}}$ radical, which covers two sites (i.e. bonded to two adjacent Pt atoms) on the surface of Pt-electrode and hence it is considered to be a strongly adsorbed intermediate. The oxidation of $(\ddot{\text{C}}\text{O})_{\text{ad}}$ is dependent on the presence of hydrous oxides, which begin to produce at 0.80V but exists significantly above 1.2 V in both acidic and neutral media. The formation of hydrous oxides and subsequent oxidation of $(\ddot{\text{C}}\text{O})_{\text{ad}}$ may be represented by the following equations [7, 20, 27-29].



The slow oxidation of $(\ddot{\text{C}}\text{O})_{\text{ad}}$ and any other inactive adsorbed species which might be formed as side product, may continue even after the appearance of forward anodic peak and results in the formation of a broad anodic peak lying just after the forward anodic peak in both acidic and neutral media.

The examination of the aforementioned mechanism indicates that overall reaction for the electro-oxidation of methanol in acidic and neutral media may be given as [30]:



The higher rate of electro-oxidation of methanol in neutral medium may be interpreted on the basis of Eq. 17 by using the fact that the H^+ ions are present in large amount in the bulk acidic solution while in neutral medium only the hydrogen ions produced during electro-oxidation of methanol accumulate along the vicinity of the electrode surface. Hence the electrochemical reaction in the forward direction is more favorable in neutral medium. It is also predicted that in basic medium, the rate of electro-oxidation of methanol may be much higher due to easier removal of hydrogen ions by OH^- ions.

4. Conclusions

The electro-oxidation of methanol on smooth platinum foil was investigated in acidic and neutral media for comparison of cyclic voltammetric characteristics and elucidation of mechanism of electro-oxidation of methanol. In both acidic and neutral media, the forward anodic peak appeared at almost the same potential of 0.85 V, which was followed by a broad anodic peak. Certain additional cathodic/ anodic peaks appeared in neutral medium, which were confirmed to arise by the reduction/oxidation of hydrogen ions produced during electro-oxidation of methanol. The exchange current densities, heterogeneous electron transfer rate constants and thermodynamic parameters ΔH^\ddagger , ΔS^\ddagger , and ΔG_{298}^\ddagger were evaluated in both acidic and neutral media. The electro-oxidation of methanol on platinum electrode was an endothermic and non-spontaneous process. The rate of electro-oxidation of methanol was higher in neutral medium as compared with acidic medium. The higher rate in neutral medium was interpreted on the basis of amount of hydrogen ions present along the surface of working electrode. The mechanism of electro-oxidation of methanol was same in both acidic and neutral media and involves the formation of various adsorbed intermediate species alongwith hydrogen ions through dissociative adsorption steps. The process of electro-oxidation of methanol was facilitated by the removal of $(\ddot{\text{C}}\text{O})_{\text{ad}}$ radicals during interaction with adsorbed hydrous oxide provided by the oxidation of adsorbed water molecules.

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