Determination of the Methanol Decomposition Mechanism on a Polycrystalline Platinum Electrode

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Abstract

Direct 4-electron and single-electron transfer mechanisms are proposed for methanol decomposition. Kinetic models showed that the water-gas shift reaction was the rate determining step for both mechanisms at E = 0.392 V vs. RHE. Single-electron transfer is more likely to occur for methanol decomposition with a Tafel slope of 212.5 mV/dec, indicating that less than 1 electron transfer was the rate determining step for 0.3-0.6 V vs. RHE.

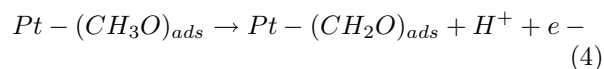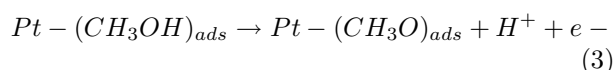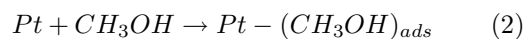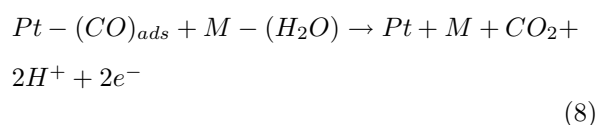**Key words:** Methanol, Decomposition, Tafel, E-transfer, Rate determining step.
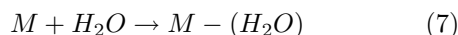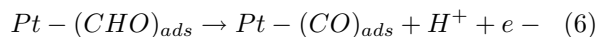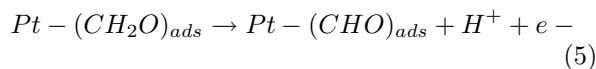
Introduction

Sluggish methanol electro-oxidation kinetics is a very important factor affecting the development of the direct methanol fuel cell (DMFC) demanded for low cost and high performance. Although a breakthrough in the understanding of the methanol electro-oxidation mechanism was obtained by techniques like in situ infrared reflectance spectroscopy, even after the results obtained during the last 20 years the methanol oxidation mechanism is still not clear. Many reactions have been proposed (Petry *et al.*, 1965; Watanabe, 1965; Bagotzky *et al.*, 1967; Biegler and Koch, 1967; Bagotzky *et al.*, 1977; Ehlers, 1985; Franaszczuk *et al.*, 1997) for the identification of the dominant mechanism for methanol oxidation like the series mechanism (Jarvi *et al.*, 1997) involving direct 4-electron transfer during decomposition of methanol and the oxidation of surface carbon monoxide by adsorbed water leading to CO_2 (regarded as the main bulk product) (Vieltich and Xia, 1995; Wieckowski, 2000) below 0.5 V.

Some differential electrochemical mass spectroscopy (DEMS) measurements also reveal a serial path on platinum electrodes below 0.45 V (Leger, 2001)

$$CH_3OH \rightarrow 4H^+ + 4e^- + CO \qquad (1)$$
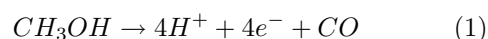
Beden et al. (2001) also proposed a detailed mechanism for the oxidation of methanol at the platinum electrode, which also forms the basis for the bifunctional mechanism for alloy catalysts. We named this mechanism the direct 4-electron mechanism for further discussion in this study;

$$Pt + CH_3OH \rightarrow Pt - (CH_3OH)_{ads} \qquad (2)$$

$$Pt - (CH_3OH)_{ads} \rightarrow Pt - (CH_3O)_{ads} + H^+ + e- \qquad (3)$$

$$Pt - (CH_3O)_{ads} \rightarrow Pt - (CH_2O)_{ads} + H^+ + e- \qquad (4)$$

$$Pt - (CH_2O)_{ads} \rightarrow Pt - (CHO)_{ads} + H^+ + e - \tag{5}$$

$$Pt - (CHO)_{ads} \rightarrow Pt - (CO)_{ads} + H^+ + e - \tag{6}$$

$$M + H_2O \rightarrow M - (H_2O) \tag{7}$$

$$Pt - (CO)_{ads} + M - (H_2O) \rightarrow Pt + M + CO_2 + 2H^+ + 2e^- \tag{8}$$

In this model, all intermediate species are assumed to occupy only 1 site on the platinum surface. In these sequences of reactions (given by Eq. (2) through Eq. (8)), M represents an alloying component or platinum metal (Frelink et al., 1995). We felt the need to show this model (given by Eq. (2) through Eq. (8), which was also proposed in our previous study (Tapan et al., 2004) in order to show the difference between single- electron transfer and the direct 4-electron transfer model where the decomposition takes place in only 1 step (Eq. (1)). In our previous study (Tapan et al., 2004) we investigated the existence of the water-gas shift reaction mechanism. In this study we tried to determine the methanol decomposition mechanism before the water-gas shift reaction.

We have proposed 2 models as the possible dominant mechanisms on the platinum surface: the direct 4-electron transfer model, which goes through Eqs. (1), (7) and Eq. (8), and the single electron transfer model, which goes through Eqs. (2)-(8).

In order to provide an insight into the true methanol oxidation mechanism, we tested the above mentioned mechanisms by first comparing the models with chronoamperometic experiments at 0.392 V vs. RHE and simulating the kinetic models for 0.392-0.6 V vs. RHE to find the rate determining steps and Tafel slopes. After we estimated the kinetic constants for these models, we determined the tafel behavior of the 2 models to discuss which mechanism holds for the studied potential range (0.3-0.6 V vs. RHE). For potentials greater than 0.6 V vs. RHE, the Tafel slope was determined by the linear sweep voltammetric technique.

We also studied methanol oxidation by cyclic voltammetry in a 3-electrode system to draw a general picture of methanol oxidation for polycrystalline platinum. The application of these methods helped us to understand the nature of methanol oxidation products on the platinum surface and the methanol oxidation mechanism.

## Experimental

Cyclic and linear sweep voltammetry

Experiments were carried out in an air sealed glass cell, which had 3 separate compartments for the working, counter, and reference electrodes. A larger area Pt foil was used as the counter electrode, and a fine porous frit was used to separate the working and counter electrode compartments. A standard calomel electrode was used for the reference electrode which was connected to the main compartment via a Luggin capillary. The working electrode was a polycrystalline platinum electrode with a 2 mm diameter that was polished with 0.1 and 0.05 μm Al_2O_3 paste and washed ultrasonically for 1 h in deionized water. All potentials were measured against a reversible hydrogen electrode.

Solutions of H_2SO_4 + CH_3OH were prepared from high purity sulfuric acid and high purity grade methanol (American Chemical Society certified methanol (99.9% pure)), and deionized water. The electrolyte was de-aerated with ultra-high-purity argon (99.999%) before and during the experiments. The experiments were carried out at room temperature (25 °C).

Cyclic voltammetry and linear sweep voltammetry experiments were performed using a CHI660 potentiostat-galvanostat controlled by PC.

Determination of active sites on the polycrystalline platinum electrode

A necessary quantitative evaluation of the chemically active surface area of the catalyst was determined from the H_{upd} charge. The H_{upd} charge was found from the cathodic potential sweep (0.4-0.05 V) during cyclic voltammetry in the acidic medium (in our previous study) (Tapan and Prakash., 2004) by the charge transfer reaction (Volmer reaction)

$$Pt + H^+ + e^- \leftrightarrow Pt - H_{ads} \tag{9}$$
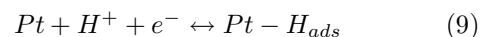
After the integration of the area under the hydrogen deposition region a total charge of 0.562 mC was obtained after subtracting the double layer contribution, the real Pt surface area Sreal = 0.562 mC/210 μC/cm^{-2}= 2.676 cm^2 and a H$_{upd}$monolayer adsorption charge of 210 μC/cm^{-2} on polycrystalline platinum were assumed. The amount of surface Pt atoms (N$_{Pt,s}$) was calculated from Faraday's law for a 1-electron reaction N$_{Pt,s}$ = 0.562 mC/96,485 C/mol = 5.831 nmol. If the total number of platinum active sites is divided by the real surface (5.831 nmol/2.676 cm^2) it gives 2.9 nmol/cm^2, which corresponds finally to 1.2 atoms/Å^2.

Chronoamperometric experiments

To measure the current transients of methanol decomposition, the following program was implemented: first, 3 activating/cleaning potential steps between the onsets of hydrogen evolution and the oxide region were applied to the electrode. The final step was applied to a measuring potential at which methanol decomposition was investigated.

After a 100 ms pre-step from 0.1 to 1.4 V (3 times), the final potential was set to a measuring potential (E$_M$) at which methanol oxidation was investigated. The oxidation currents were recorded for 1 s at the applied potential in a 0.5 M H$_2$SO$_4$ electrolyte for the baseline correction and a 0.5 M CH$_3$OH + 0.5 M H$_2$SO$_4$ solution for methanol oxidation investigation. Each chronoamperometric experiment was repeated at least 10 times and corrected for the baseline, and average current values were recorded. Standard deviations were within 10% for the 10 chronoamperometric measurements.

Results and Discussion

Cyclic voltammetry

Cyclic voltammetry experiments were performed on a polycrystalline platinum electrode in argon saturated 0.1 M H$_2$SO$_4$+CH$_3$OH at 25 °C. Figure 1 shows the cyclic voltammogram before and after addition of 1 ml of methanol to the electrolyte.

Figure 1 (black line) shows the reactions on the platinum: a/a$^{'}$and b/b$^{'}$ show the adsorption and desorption of the hydrogen atom, and c/c$^{'}$ shows the formation ($\sim$0.8 V) and reduction of platinum oxide ($\sim$0.7 V). There are 2 peaks observed for the hydrogen adsorption-desorption region; the first ($\sim$0.04 V) and second ($\sim$0.3 V) correspond to the weakly and

strongly adsorbed hydrogen atom respectively (Kinoshita and Stonehart 1986). After methanol was injected into the electrolyte, we observed that strongly adsorbed hydrogen diminished and 3 distinct (irreversible) peaks appeared at potentials $\sim$0.6, $\sim$0.75 and 1.4 V. As seen in the platinum oxidation regime, activation increased after the addition of methanol. The peak around 0.75 V was assigned to the decomposition of methanol to carbon monoxide. The third (1.4 V) and first (0.6 V) peaks were assigned to the oxidation of linear bonded carbon monoxide (Wieckowski, 2000).
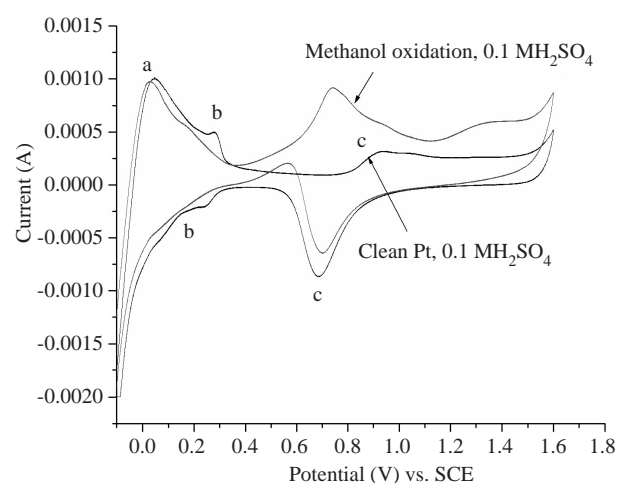

Figure 1. Cyclic voltammograms for a polycrystalline Pt electrode at a scan rate of 100mV/s.

In order to understand more about the nature of oxidation products we decided to see where the first peak appears (or where the surface species form). In order to accomplish this, we increased the potential scan window until the first peak appeared.

It can be seen from Figure 2 that the onset of methanol oxidation is $\sim$0.6 V and the first peak appears between 1 and 1.4 V. This may be due to the formation of a negligible amount of surface species before 1 V vs. RHE, and the active platinum surface may be free of decomposition products, but the formation of soluble species may be high.

Model

Some assumptions were made before the simulation of 3 step and 7 step methanol oxidation mechanisms. A Langmuirian type of adsorption for methanol and water was assumed. The oxidation mechanism was studied in a pure kinetic region since the highest current achieved from chronoamperometric experiments

was 0.05 mA/cm^2, which is 3 orders of magnitude lower than the diffusion controlled current (for a 0.5 M CH$_3$OH solution diffusion effects are not negligible in the current range of 100 mA/cm^2) (Hoster *et al.*, 2001).
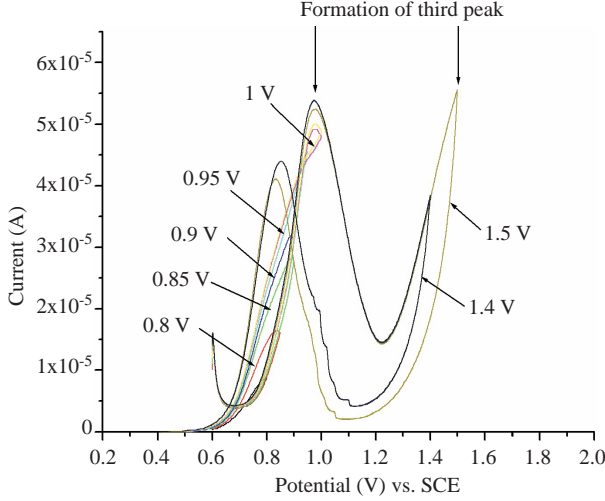

Figure 2. Cyclic voltammograms for a Pt electrode at a scan rate of 1 mV/s in 0.5 M H$_2$SO$_4$+ 0.5 M CH$_3$OH.

Derivation of model equations

The development of the model equations was taken from our previous research and details of the model development can be found in Tapan and Prakash (2005). In order to derive species balances we started with the definition of Faraday's law, where the current can be expressed in terms of a rate of change of electroactive species

$$i = F.n_{eq}.\frac{dN}{dt} \qquad (10)$$

where N is the number of moles of species, n_{eq} is the number of equivalence and F is Faraday's constant.

After that we converted the faradaic current in terms of coverages of each electroactive species on the metal surface (Eq. (11))

$$\frac{i}{F.n_{eq}.N_t} = \frac{d(N/N_t)}{dt} = \frac{d\theta_i}{dt} = \frac{A}{N_t}.\left(\sum \nu_i.k_i.\theta_i\right) \qquad (11)$$

In Eq. (11) N_t represents the number of active metal surface atoms, θ_i represents the coverage of electroactive species, A is the area of the electrode,

ν_i is the stoichiometric coefficient of input and output terms to the accumulation of species coverages, and k_i is the rate constant of the specific oxidation or adsorption reaction.

Each electron transfer step in the 2 mechanisms can be regarded as creating a faradaic current. The total current can therefore be expressed as the sum of individual e-transfer steps in the mechanism. The net faradaic current can therefore be defined for the 2 mechanisms as in Eq. (12) (representing direct 4-electron transfer) and Eq. (13) (representing single electron transfer)

$$I_{\text{NET},4-etransfer} = I_{EX0} + n.F.k_{WGS}.\theta_{H2O}.\theta_{CO}.$$
$$\exp((1-\beta).F.\eta/(R.T)) + n.F.k_{CO}.\theta_{CH3OH}.$$
$$\exp((1-\beta).F.\eta/(R.T)) \qquad (12)$$

$$I_{\text{NET, single}-etransfer} = I_{EX0} + n.F.k_{WGS}.\theta_{H2O}.\theta_{CO}.$$
$$\exp((1-\beta).F.\eta/(R.T)) + \Sigma n_i.F.k_i.\theta_i.$$
$$\exp((1-\beta).F.\eta_i/(R.T)) \qquad (13)$$

Block diagrams used to derive Eqs (12) and (13) are given in Figures 3 and 4, These two figures focus on the difference between the decomposition steps of the 2 mechanisms.
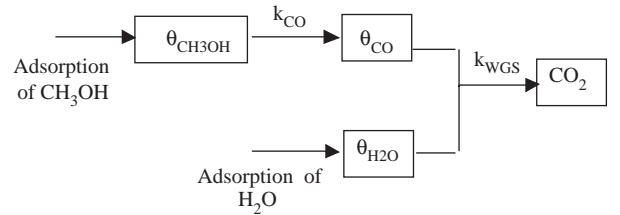

Figure 3. Block diagram of the direct 4-electron transfer mechanism.
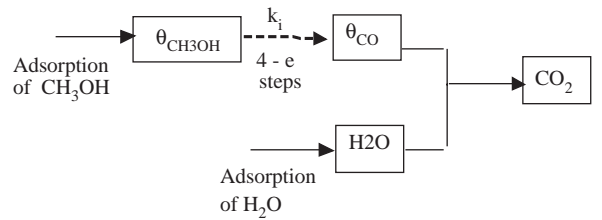

Figure 4. Block diagram of the single electron transfer mechanism.

In these 2 equations I_{EX0} stands for the current leading to soluble product formation such as formic acid and formaldehyde (Wieckowski, 2000) in a 0-40 ms interval; η is the overpotential, which is the difference between the applied potential and standard potential of the electrochemical step (Tapan, 2003); and β is the symmetric factor, which is 0.5 for most electrochemical systems of interest (Bard, 2001). Net faradaic currents given by Eqs. (12)-(13) were a result of numerical integration from simulation. After numerical integration, the net faradaic currents of the 2 models were compared using chronoamperometric experiments (Figures 5, 6) at 0.392 V vs. RHE, and the kinetic constants were estimated. We applied a trial and error procedure to the kinetic rate constants until the 2 models fitted perfectly, within 10% error, to the chronoamperometric data (Tables 1, 2). The order of magnitude of kinetic rate constants was unique for the 2 models. Our approach to estimating the rate constants is shown in Figure 7. When we ran the simulation for the 2 models for one second, they both showed that the faradaic current for the water-gas shift reaction was rate determining, and so the 2 models predicted that soluble product formation to carbon-dioxide would be low (Figures 8, 9). This result agrees with our previous research (Tapan and Prakash, 2005) where the dynamic profiles between 0.348 and 0.592 V vs. RHE show the water-gas shift reaction has the lowest electrochemical activity.

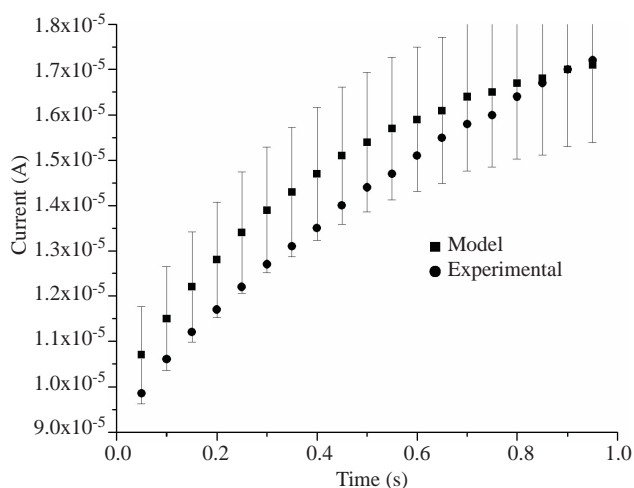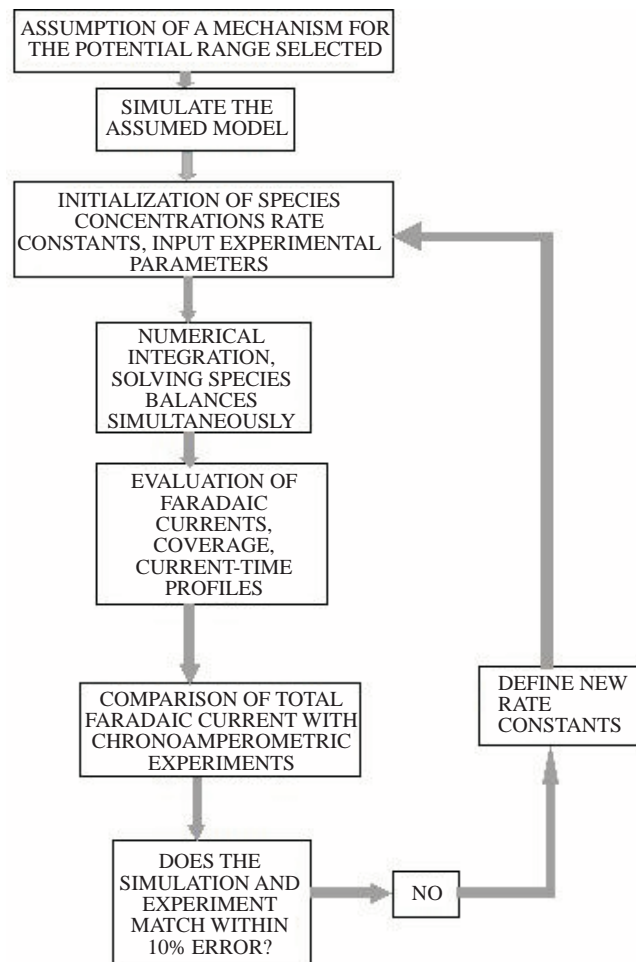**Figure 6.** Schematic representation of method of approach.

Figure 5. Comparison of 3-step model with chronoamperometric experiment at E = 0.392 V vs. RHE.
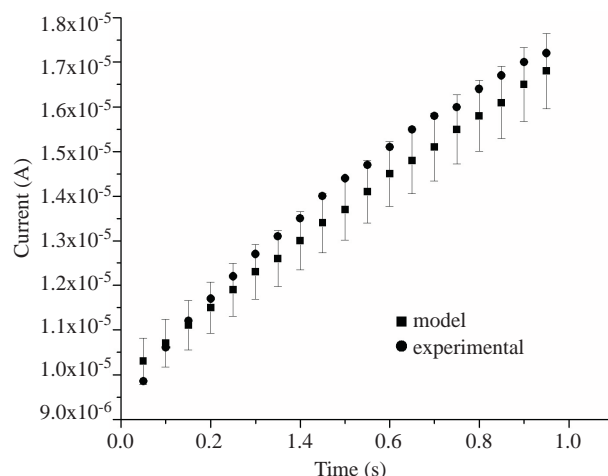

Figure 7. Comparison of 7-step model with chronoamperometric experiment at E = 0.392 V vs. RHE.

Table 1. Estimated kinetic constants for E = 0.392 V vs. RHE.

Rate Constant	7-step	3-step
Methanol adsorption (s^{-1})	4.2×10^{-8}	4.2×10^{-8}
Decomposition (k$_{CO}$), (s^{-1})	5.5×10^{-5}	1.3×10^{-8}
Water adsorption (s^{-1})	4.2×10^{-10}	4.2×10^{-10}
Shift reaction (k$_{WGS}$) coverage^{-1}.s^{-1})	4.2×10^{-8}	4.2×10^{-8}

Table 2. Comparison of experimental and model time dependent currents.

Time(s)	I$_{exp}$(A)	I$_{3-STEP}$(A)	% error	I$_{7-STEP}$(A)	% error
0.05	9.86×10^{-5}	1.07×10^{-5}	8.5	1.03×10^{-5}	4.5
0.1	1.06×10^{-5}	1.15×10^{-5}	8.5	1.07×10^{-5}	0.9
0.15	1.12×10^{-5}	1.22×10^{-5}	8.9	1.11×10^{-5}	0.9
0.2	1.17×10^{-5}	1.28×10^{-5}	9.4	1.15×10^{-5}	1.7
0.25	1.22×10^{-5}	1.34×10^{-5}	9.8	1.19×10^{-5}	2.5
0.3	1.27×10^{-5}	1.39×10^{-5}	9.4	1.23×10^{-5}	3.1
0.35	1.31×10^{-5}	1.43×10^{-5}	9.2	1.26×10^{-5}	3.8
0.4	1.35×10^{-5}	1.47×10^{-5}	8.9	1.30×10^{-5}	3.7
0.45	1.40×10^{-5}	1.51×10^{-5}	7.8	1.34×10^{-5}	4.3
0.5	1.44×10^{-5}	1.54×10^{-5}	6.9	1.37×10^{-5}	4.9
0.55	1.47×10^{-5}	1.57×10^{-5}	6.8	1.41×10^{-5}	4.1
0.6	1.51×10^{-5}	1.59×10^{-5}	5.3	1.45×10^{-5}	4.0
0.65	1.55×10^{-5}	1.61×10^{-5}	3.8	1.48×10^{-5}	4.5
0.7	1.58×10^{-5}	1.64×10^{-5}	3.8	1.51×10^{-5}	4.4
0.75	1.60×10^{-5}	1.65×10^{-5}	3.1	1.55×10^{-5}	3.1
0.8	1.64×10^{-5}	1.67×10^{-5}	1.8	1.58×10^{-5}	3.6
0.85	1.67×10^{-5}	1.68×10^{-5}	0.6	1.61×10^{-5}	3.6
0.9	1.70×10^{-5}	1.70×10^{-5}	0	1.65×10^{-5}	2.9
0.95	1.72×10^{-5}	1.71×10^{-5}	0.6	1.68×10^{-5}	2.3
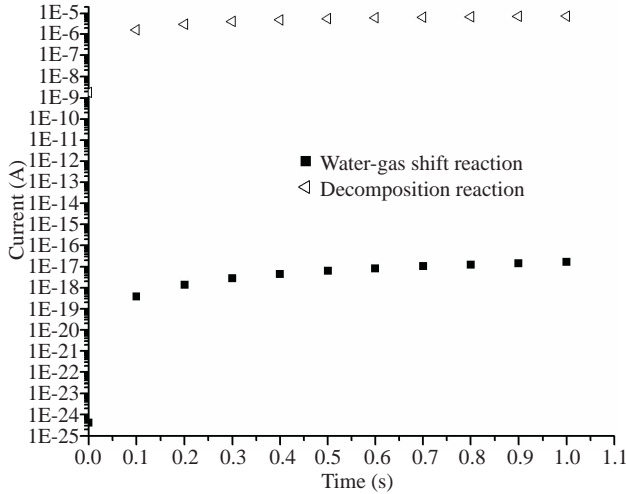
Figure 8. Magnitudes of electrochemical reactions during methanol oxidation for 3-step model, E = 0.392 V vs. RHE.
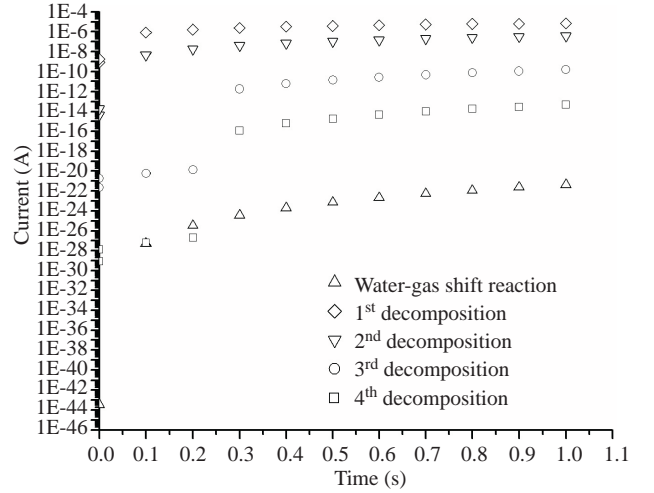
Figure 9. Magnitudes of electrochemical reactions during methanol oxidation for 7-step model, E = 0.392 V vs. RHE.

Tafel slopes

In order to find the leading mechanism in methanol electrooxidation we determined the Tafel slopes of 2 proposed mechanisms (direct 4-electron transfer and single electron transfer) by simulating the region 0.3-0.6 V vs. RHE and 0.6 (the onset of methanol oxidation)-0.85 V (first oxide formation on polycrystalline platinum) experimentally by staircase voltammetry. We simulated the region 0.3-0.6V vs. RHE because it was not possible to observe the region in detail by electrochemical means (Figures 1, 2).

In order to study the mechanism of methanol electro-oxidation, we determined the Tafel slope using the following equation:

$$\eta = A + b \log i \tag{14}$$

where η is the overpotential and b is the Tafel slope given by

$$b = \frac{RT}{\alpha nF} = \frac{60mV/dec}{\alpha} \tag{15}$$

and α is the transfer coefficient. The transfer coefficient may be calculated using

$$\alpha = \frac{\gamma}{\nu} + \rho\beta \tag{16}$$

where γ is the number of steps preceding the rate determining step, ν is the stoichiometric coefficient (1 for the given mechanism), and ρ equals 0 when the rate determining step is a chemical step and 1 if the rate determining step is an electron transfer step.

When we assumed that the direct 4-electron transfer mechanism holds for methanol oxidation and simulated the region between 0.3 and 0.6 V vs. RHE, the Tafel slope was 32 mV/dec (Figure 10). This value was close to 30 mV/dec, which shows that the rate determining step is the second chemical reaction step (based on Eq. (16)). The second chemical step in the direct 4-electron step may be the adsorption of water or methanol.

On the other hand, when we assumed the single electron transfer mechanism as a dominant mechanism for methanol oxidation, the Tafel slope was 212.5 mV/dec (Figure 11), which was close to 120 mV/dec, indicating a first electron transfer step. A first electron transfer step may be the decomposition of adsorbed methanol in the single electron transfer

mechanism. In the literature, polycrystalline platinum data at room temperature showing a steeper Tafel slope were mentioned (Lipkowski and Ross, 2001) below 0.5 V vs. RHE, indicating a rate determining step involving a less than 1 electron transfer step or a change in the reaction mechanism over the indicated potential range. The possibility of the change in the rate determining step (from a water-gas shift to third decomposition and CO formation) at 0.45 V was discussed in our previous research. (Tapan et al., 2004) This information makes a single electron transfer model more likely to occur before 0.6 V vs. RHE.
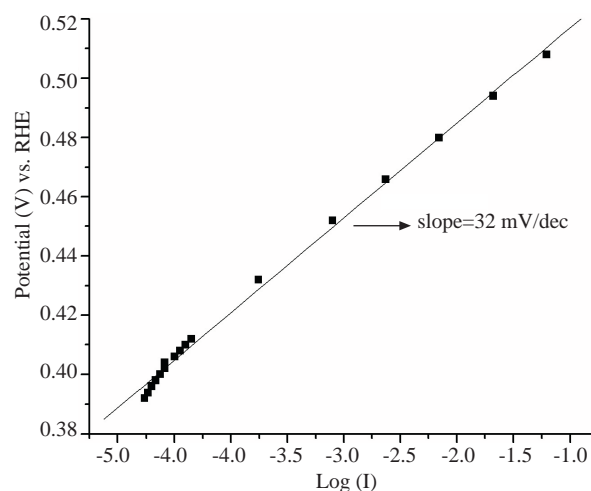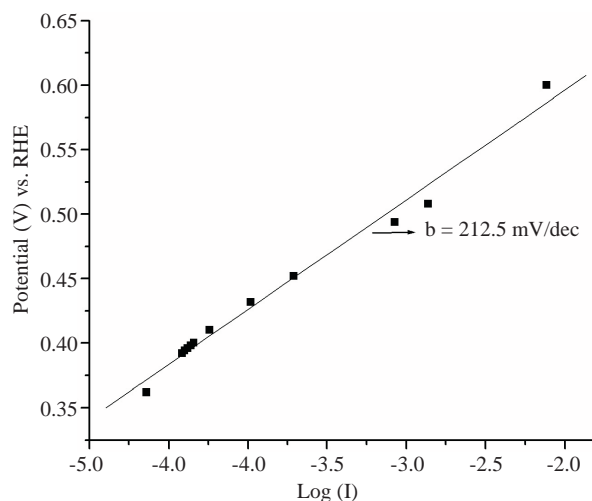

Figure 10. Tafel slope for 3-step mechanism.

Figure 11. Tafel slope for 7-step mechanism.

By using linear sweep voltammetry, the Tafel slope was found to be 107.8 mV/dec (close to 120 mV/dec) in the region between 0.6 and 0.85V vs.

RHE (Figure 12) This indicates that the first electron transfer is the rate determining step for potentials greater than 0.6 V vs. RHE (based on Eq. (16)). Since there is no single electron transfer step in the direct 4-electron transfer model (see Eq. (1)) (or to put it another way, decomposition of methanol occurs all at once in a direct 4-electron transfer mechanism), a single electron transfer mechanism is more likely to occur.
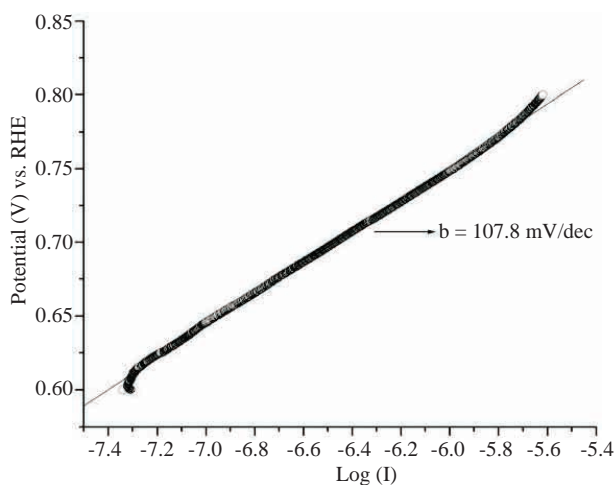

Figure 12. Staircase voltammetry for a Pt electrode at a scan rate of 1 mV/s in 0.5 M H$_2$SO$_4$ + 0.5 M CH$_3$OH, forward scan from the hydrogen underpotential deposition region. Tafel slope analysis.

Conclusions

Cyclic voltammetry showed that the main surface species on polycrystalline platinum may appear after 1 V vs. RHE. Although dynamic simulation at 0.392 V vs. RHE showed that the water-gas shift reaction was the rate determining step for direct 4-electron transfer and a single electron transfer model, Tafel slopes in the region of 0.3-0.6 V vs. RHE were 32 mV/dec for direct 4-electron transfer and 212.5 mV/dec for single electron transfer mechanisms, indicating a second chemical step and first electron transfer steps as rate determining steps. Using staircase voltammetry, the Tafel slope in the region of 0.6-0.85 V vs. RHE was found to be 104 mV/dec, indicating a first electron transfer (methanol decomposition) as a rate determining step. The 7-step model is more likely to occur than direct 4-electron transfer before and after 0.6 V vs. RHE.

Nomenclature

β	symmetric factor
η	overpotential V
F	Faraday's constant 96,500 coulomb/mole equivalent
I	current A
k$_i$	kinetic constant s^{-1}
N$_t$	total number of surface atoms
n$_{eq}$	# of equivalence
θ	coverage
R	ideal gas constant kJ/mol.K
RHE	reversible hydrogen electrode

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