

# Investigation of Methanol Oxidation Electrokinetics on Pt Using the Asymmetric Electrode Technique

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**Abstract:** The performance of a commercial Pt-black electrocatalyst was investigated in a Direct Methanol Fuel Cell (DMFC). A method for establishing the validity of anode polarization (without the use of a reference electrode) was shown by purging hydrogen and argon gas at the cathode under an asymmetric electrode configuration. It was found that hydrogen crossover to the cathode has a negligible effect on the polarization curve. In order to study methanol oxidation kinetics, the effects of mass transfer and ohmic resistances are eliminated and the correction techniques are discussed. At  $\approx 0.55$  V,  $E_a$  changes from 60 kJ/mol to 40 kJ/mol (the removal of surface carbon monoxide) which points to the change in the rate determining step of the methanol oxidation reaction. Based on the value of the Tafel slope (138 mV/dec), the rate-determining step on the platinum surface can be the first electron transfer step (first C-H bond breakage of methanol or the activation of water) before 0.55 V.

**Keywords :** Direct Methanol Fuel Cell, Asymmetric Electrodes, Methanol Oxidation Kinetics

## 1. INTRODUCTION

Fuel cells are electrochemical devices that convert the chemical energy of a fuel source directly into electrical energy. The DMFC is a type of Proton Exchange Membrane (PEM) fuel cell where liquid methanol is fed directly into the fuel cell anode as the fuel source. It is widely known that a liquid fuel would have very convenient storage and handling properties (atmospheric pressures, low temperatures) when compared to hydrogen, which would greatly simplify the on-board fuel storage and treatment system [1] as well as the infrastructure needed to transport and distribute the fuel. The distribution infrastructure and safety concerns are so crucial that they constitute two of the largest barriers in the development of a hydrogen economy. Therefore, the operation of a liquid fuel cell that exhibit a sim-

ilar performance to that of the hydrogen fuel cell would assist in expediting the introduction of the fuel cell into commercial markets, most notably the automotive industry.

The basic physical structure of a PEM fuel cell consists of a solid electrolyte layer in contact with porous electrodes located on both the anode and cathode sides. The electrolyte in the PEM is a solid polymer ion exchange membrane (typically fluorinated sulfonic acid polymer or other similar polymer), which serves the dual purpose of an excellent proton conductor and an electrical insulator. Due to its natural abundance, oxygen is supplied to the cathode where its acidic media reduction reaction occurs. Again, in the DMFC, methanol is directly fed into the anode where its oxidation reaction takes place.

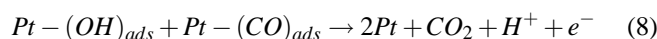
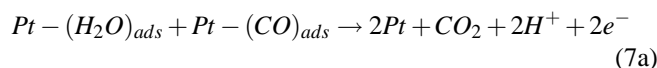
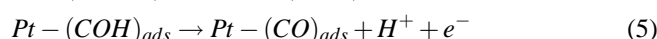
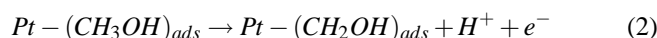
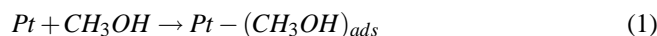
The first promising performance characteristic for the methanol fuel cell lies in the thermodynamic potential of methanol, which is extremely close to the reversible potential for hydrogen. An-

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other preferable feature of the DMFC is that methanol has a superior energy density (167 kcal/mol) for 100% conversion to CO<sub>2</sub> when compared with hydrogen (57 kcal/mol) [3]. This was recognized as early as the 1920's [2] and drew much attention to methanol as a possible energy source. These two features alone give the DMFC the potential to be a fuel that not only meets the performance of the hydrogen fuel cell, but also exceeds it.

On the other hand, there are several issues with the DMFC that need to be addressed. The three main performance problems involve methanol crossover to the cathode, high activation overpotentials and CO poisoning of the negative electrode catalyst surface (traditionally platinum). Extensive research has been done to develop more advanced electrolyte materials to combat fuel crossover [19, 22, 25] and more active anode catalysts to promote methanol oxidation.

In order to expedite the development of superior alloy catalysts, the overall mechanism should be well known [4,5]. Therefore, the methanol oxidation mechanism has been extensively studied [6-17]. It has been shown that the bifunctional model, along with the Eley-Rideal mechanism, is sufficient to describe methanol oxidation [4, 17, 18]. The bifunctional model is detailed in Equations 1-8.



The mechanism above is typically described as a parallel mechanism. Though steps 1 through 5 happen sequentially, steps 1 and 6 happen simultaneously. This means that in any system either step could be considered the first step in the overall mechanism. Therefore, steps 2, 7a and 7b could all be considered the first electron transfer step in the complete electrochemical oxidation of methanol to CO<sub>2</sub>.

## 2. EXPERIMENTAL

The anode polarization experiments were performed under asymmetric electrode conditions (Figure 1). Humidified hydrogen and argon were purged (1.0 mL/min) through the cathode compartment of the fuel cell, whose geometric electrode area was

5cm<sup>2</sup>. Methanol was peristaltically pumped through the anode (1 M, 2.8 mL/min), with an area of 0.36cm<sup>2</sup>. The asymmetric electrode configuration is shown in Figure 2 where it is contrasted with the typical symmetric electrode setup.

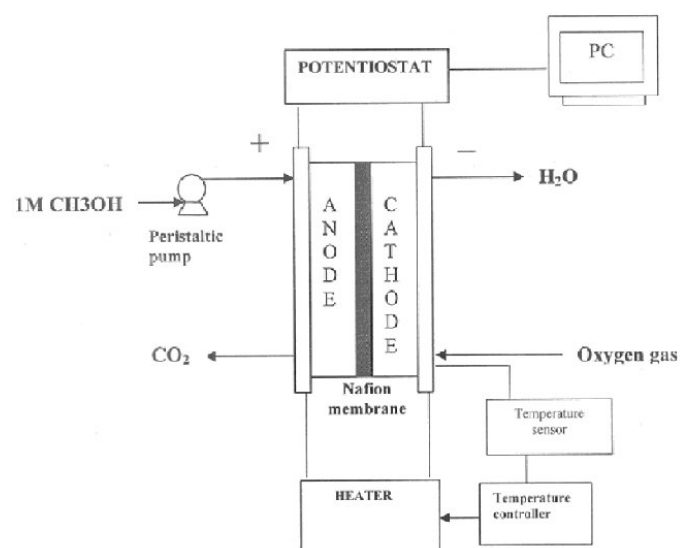


Figure 1: Schematic representation of experimental DMFC setup.

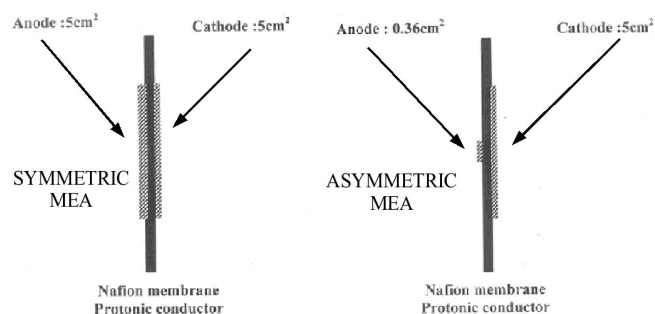


Figure 2: Demonstration of symmetric and asymmetric electrode configurations.

All catalyst (Johnson Matthey, E-TEK Pt black) loadings were 4mg Pt/cm<sup>2</sup>. The anode electrodes consisted of a thin carbon paper (100 microns) that was painted with a 12 weight percent (wt %) Nafion Pt black catalyst ink. The cathode was constructed of a thin, teflonized (20 wt %) carbon paper and painted with 15 wt % Nafion and 12 wt % PTFE Pt black catalyst ink. The electrodes were painted and dried until desired catalyst loadings were achieved.

To obtain optimal performance, the Nafion 117 membranes were extensively pretreated before use. The membrane pretreatment

involved repeated boiling of the membranes for at least 1 hour in the following solutions: 3 wt %  $\text{H}_2\text{O}_2$  (Aldrich), 18 m $\Omega$  Millipore water and 0.5 M  $\text{H}_2\text{SO}_4$  (Aldrich). After pretreatment of the membranes and the preparation of carbon-paper supported catalyst electrodes, the electrodes were hot pressed [20-22]. The fuel cell was then heated to the desired operating temperature and Millipore water was passed through the anode for 48 hours to ensure membrane hydration.

All polarization and chronoamperometric experiments were conducted using an Autolab PGSTAT30 potentiostat. Cyclic voltammetry was carried out in the potential regime of 0.05-0.815 V at a scan rate of 0.417 mV/sec. Forward and reverse scans were examined at temperatures 31-80°C.

### 3. RESULTS AND DISCUSSION

#### Hydrogen Crossover

Due to the porosity of the Nafion membrane, it is quite conceivable [26,27] that the flow of  $\text{H}_2$  through the cathode compartment may lead to hydrogen crossover, which may falsely enhance the methanol oxidation kinetics, thereby compromising the validity of any anode polarization experiment where  $\text{H}_2$  is used in the cathode compartment. In order to evaluate if hydrogen crossover has any effect on the anode polarization, both hydrogen and an inert gas (in this case argon) must be purged through the cathode compartment and their anode polarization results compared. The results are shown in Figure 3.

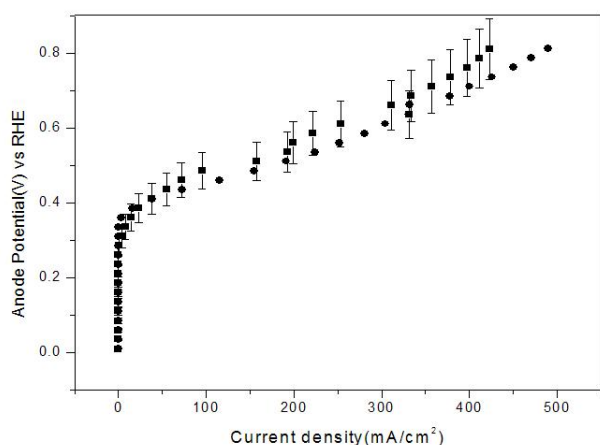


Figure 3: Pt anode polarization curves at 80°C, purging argon and hydrogen in the cathode compartment. (●) Hydrogen; (■) Argon

There appears to be little deviation between the experimental results for either case. This indicates that either  $\text{H}_2$  crossover

does not occur or that it has virtually no effect on the anode polarization curve. Either way, it can be concluded that hydrogen is an acceptable cathode compartment gas for the asymmetric electrode experiments and was used for all anode polarization curves reported. Polarization curves were obtained at several temperatures ranging from 32 to 80°C and are presented as Figure 4.

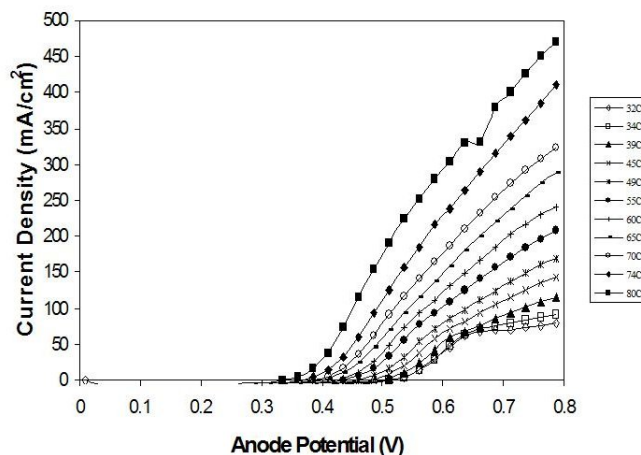


Figure 4: Uncorrected Pt black anode polarization curves for temperatures between 32 and 80°C.

#### Correction for Ohmic and Mass Transfer Resistance

The data shown in the aforementioned figure has a number of components, namely the effects of kinetic, ohmic and mass transfer resistance. In order to divulge the pure kinetic behavior, the data must first be corrected for the other two resistances.

The first resistance that will be discussed is ohmic (cell) resistance. To compensate for this during anode polarization, the current interruption technique was used (Figure 5). The basic premise of this technique is to induce a current step from a given value to zero and record the cell voltage response as a function of time. When the current is dropped to zero, the cell voltage first drops because of IR (uncompensated resistance), followed by a monotonic decrease due to the double layer discharging and other processes. However, due to the relaxation of the double layer, it can be difficult to determine the quantitative value for the IR drop. To elucidate this effect, the experiment has been performed at several currents. A linear relationship has been found between the applied current and the uncompensated resistance, which indicates that the effect of the double layer is negligible and the value obtained can be taken as the pure ohmic cell resistance.

The other resistance that is corrected for is the mass transfer resistance. The mass transfer correction was made using the

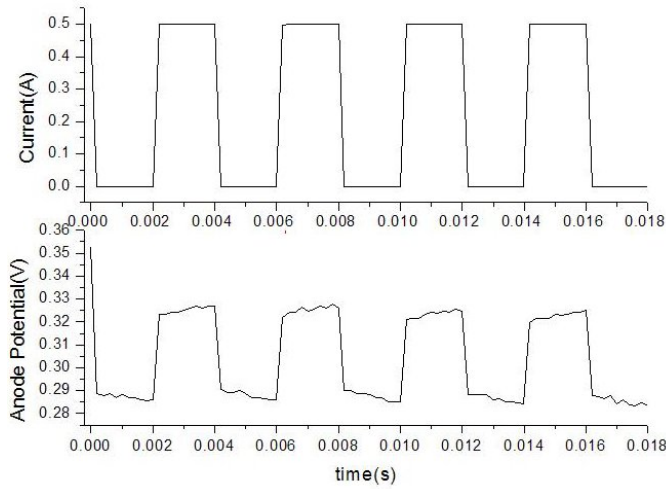


Figure 5: Current interruption experimental results at 0.5A and 80°C.

limiting current determined by the non-linear regression method given by Squadrito et al [23]. After finding the limiting current, the kinetic current,  $I_k$ , can be found according to the following expression:

$$I_k = \frac{I_L I}{I_L - I} \quad (9)$$

where  $I_L$  is the limiting current and  $I$  is simply the current after correction for the ohmic resistance. The ohmic and mass transfer corrected plot is given as Figure 6.

### Activation Energy

Utilizing the results from Figure 6, we are able to determine the activation energy for the methanol oxidation reaction in the fuel cell. Using the corrected values for the kinetic current, the activation energy can be calculated using an Arrhenius style equation

$$I_k = k_o \exp \left[ \frac{-E_a}{RT} \right] \quad (10)$$

where  $I_k$  is the kinetic current,  $E_a$  is the activation energy,  $R$  is the ideal gas constant,  $T$  is the temperature and  $k_o$  is the pre-exponential factor. Activation energy values were calculated by plotting  $\ln I_k$  versus  $1/T$  [Figure 7], where  $E_a/R$  is equal to the slope of the linear curve.

For the Pt black electrode, the activation energy splits into two distinct groups. Up to 0.55V, the methanol oxidation gives an activation energy value of approximately 60 kJ/mol. However,

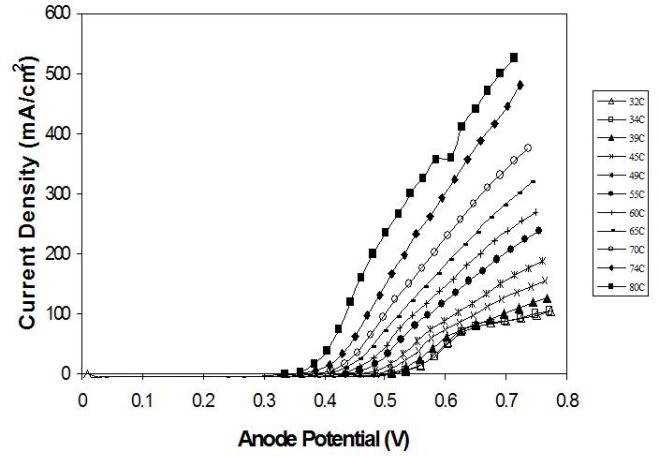


Figure 6: Mass transfer and ohmic resistance corrected anode polarization curve for Pt black anode electrode at various temperatures.

following 0.55 V, values close to 40 kJ/mol are calculated. This drastic decrease in activation energy is most likely related to a change in the rate-determining step.

### Tafel Slope Analysis

In order to study the mechanism of methanol electrooxidation, we have determined the Tafel slope using the following equation

$$\eta = A + b \log i \quad (11)$$

where  $b$  is given by

$$b = \frac{RT}{\alpha nF} = \frac{60mV/dec}{\alpha} \quad (12)$$

and  $\alpha$  is the transfer coefficient. The transfer coefficient may be calculated using

$$\alpha = \frac{\gamma}{\nu} + \rho\beta \quad (13)$$

where  $\gamma$  is the number of steps preceding the rate determining step,  $\nu$  is the stoichiometric coefficient (1 for the given mechanism),  $\rho$  equals 0 when the rate determining step is a chemical step and 1 if the rate determining step is an electron transfer step and  $\beta$  is the symmetric factor, which is 0.5 for most systems of interest [24].

Tafel analysis for the asymmetric platinum electrode at 80°C indicates a Tafel slope of 138 mV/dec [Figure 8] between the

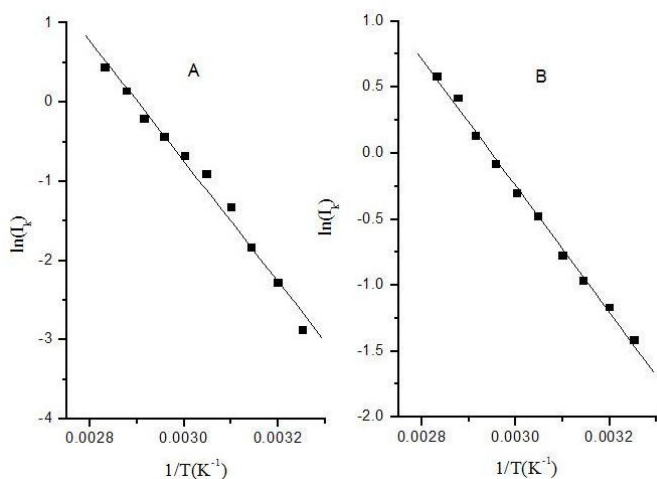


Figure 7: Arrhenius plots for Pt anode polarization for (A)  $E < 0.55\text{V}$  and (B)  $E > 0.55\text{V}$  vs RHE.

open circuit potential (OCV) and 0.5 V, which is close to a 120 mV/dec slope that would indicate that the first electron transfer is the rate-determining step in that region. This observed Tafel region falls below 0.55 V, where the activation energy showed a significant change. Since the methanol electrokinetics is quite slow at potentials less than 0.55 V, it is reasonable to deduce that before 0.55 V, the rate-determining step is the first C-H bond breakage, producing  $\text{H}^+$  and  $\text{e}^-$ . No Tafel region was observed at potentials greater than 0.55 V due to the instability of the calculated values. Therefore, we may only attempt to determine the rate-limiting step based on the value obtained for the activation energy. The activation energy value of 39.94 kJ/mol is consistent with those reported for the removal of CO [17] hence suggesting the removal of adsorbed CO as the rate-determining step at potentials greater than 0.55 V.

#### 4. CONCLUSIONS

It has been shown that hydrogen crossover has no appreciable effect on the asymmetric electrode anode polarization curves. The polarization curves have been obtained for several temperatures between 32°C and 80°C. These curves were corrected for both ohmic and mass transfer resistances. This has allowed for the computation of both activation energies and Tafel slopes.

A critical potential is observed around 0.55 V. Before this potential, first C-H bond breakage step, producing  $\text{H}^+$  and  $\text{e}^-$ , appears to be the rate-determining step. Though no different Tafel region is observed at potentials greater than the critical potential, the magnitude of the activation energy suggests that the removal of adsorbed CO becomes rate-limiting.

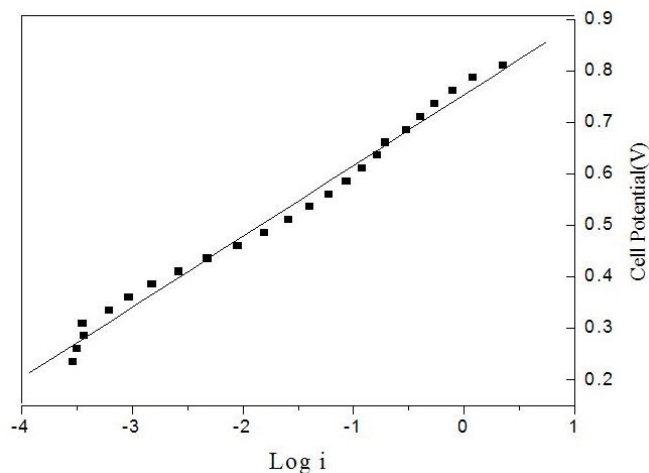


Figure 8: Tafel curve for asymmetric Pt electrode at 80°C.

#### LIST OF SYMBOLS

Symbol	Definition
$\beta$	symmetric factor
$\eta$	overpotential (V)
$E_a$	activation energy of adsorption(kJ/mol)
$I_L$	limiting current ( $\text{mA}/\text{cm}^2$ )
$I_k$	kinetic current ( $\text{mA}/\text{cm}^2$ )
$R$	ideal gas constant (kJ/mol.K)
$k_o$	pre-exponential factor
$b$	tafel slope (mV/dec)
$n$	# of equivalence
$\alpha$	transfer coefficient
$\rho$	constant for chemical or electrochemical step (0 or 1)
$\gamma$	# of steps preceding rate determining step
$\nu$	stoichiometric coefficient
$F$	faradays constant (96500 coulomb/mole equivalent)

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