CHAPTER 4

MODEL DEVELOPMENT

4.1 Introduction

In this chapter, a mathematical model for air breathing microfluidic fuel cell is developed to study the effects of fuel concentration, and temperature on the cell voltage when current is drawn from the cell. All three fuels methanol, ethanol and sodium borohydride are considered for the estimation of different types of overpotentials at anode via model equations systematically. For the cathode overpotentials oxygen was considered as oxidant. The mathematical model is developed to estimate the over potentials of cell under different operating conditions. The model is developed taking into account all the losses, e.g. activation (η_{act}), ohmic (η_{ohm}), and concentration (η_{con}) over potentials at anode and cathode, respectively. When current is drawn from the fuel cell, the cell voltage will drop due to various irreversibilities occurs at the electrodes. The irreversibilities or losses are often called overpotential or polarization, . Thus, at any current density operating cell voltage, E_{cell} is calculated from the following equation:

$$E_{cell} = E - \eta \tag{4.1}$$

Where E is the theoretical open circuit potential at no current.

The performance of the fuel cell is generally reduced due to the losses of some electrical energy to drive the oxidation and reduction reaction at the anode and cathode and the losses are known as activation overpotential (η_{act}), ohmic overpotential (η_{ohm}) is due to losses of

different resistances across electrolyte, current collectors, and interconnects etc. and mass transfer resistance(η_{con}) at the anode and cathode is known as concentration overpotential. Activation overpotential is primarily responsible for voltage loss at low current density, ohmic resistance is responsible for voltage loss at intermediate range of current density, whereas concentration overpotential is mainly responsible for voltage loss at a high current density. Thus equation (4.1) is written as,

$$E_{cell} = E - (\eta_{act} - \eta_{ohm} - \eta_{con}) \qquad (4.2)$$

The assumptions of the mathematical model are:

   I.   Neglecting the body forces and heating due to viscous dissipation at a low velocity.

  II.   The flow of the fuel and oxidizer streams are in the laminar region.

 III.   The relative velocity of the two streams in contact with each other at the interface is assumed zero when they flow side by side through the microchannel.

 IV.   Pressure is 1 atm

  V.   The transport process is represented by one dimensional equation

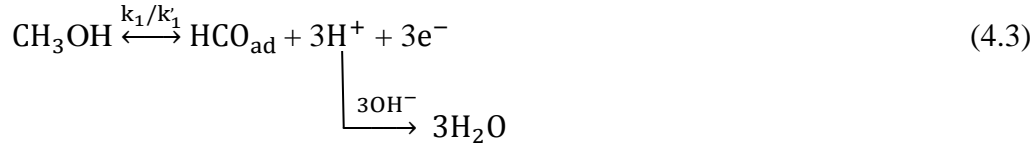 VI.   Activation overpotential at cathode is neglected

In the following sections, the individual overpotentials are discussed, and the mathematical expressions for each loss for air breathing microfluidic fuel cell using methanol, ethanol and sodium borohydride at anode and oxygen/air at the cathode are derived.

4.2 Activation Overpotentials

The activation overpotential is directly related to the reaction kinetics. These are caused by the slowness of the reaction on the surface of the electrodes. The activation overpotential is a portion of the voltage generated that is lost in driving the chemical reaction that transfers the electrons to or from the electrode. Activation overpotential is directly related to the electrochemical reactions kinetics as the reaction propagates at the rate demanded by the specific load. When there is no load on the cell, oxidation reduction reaction reaches equilibrium at the electrode. The current density related to electron transfer in such reactions in known as exchange current density (i_o). Many investigators, (Takasu et al. 2000, Guo et al. 2005, Santos et al. 2006) reported that the oxygen reduction kinetics on Pt electrocatalyst is excellent. Thus, it is assumed that the activation over potential at the cathode is less significant compared to that at the anode. The model developed for theoretical prediction of activation overpotential is discussed below for methanol, ethanol, and sodium borohydride fuels.

4.2.1   Methanol ($\eta_{a,act,MeOH}$)

The electrooxidation reaction mechanism of methanol is proposed by Tripkovic et al. (2001) is used to model the activation overpotential. The end product of methanol electrooxidation reaction is formic acid. However, in alkaline medium formic acid exists in the form of formate ion, which is discussed in half-cell analysis section (Page no. 37). Except for formic acid, a few poisoning species carbon monoxide is also produced that is neglected in the model development. The reaction mechanism proposed by Tripkovic et al. (2001) is as follows:

$$CH_3OH \xrightarrow{k_1/k_1'} HCO_{ad} + 3H^+ + 3e^- \qquad (4.3)$$

$$\xrightarrow{3OH^-} 3H_2O$$

$$OH^- \xrightarrow{k_2/k_2'} + OH_{ad} + e^- \qquad (4.4)$$

$$HCO_{ad} + OH_{ad} \xrightarrow{k_3} HCOOH \qquad (4.5)$$

Where k_1, k_2, and k_3 are the rate constant for the forward reactions in equation (4.3) to

(4.5), k_1' and k_2' are the rate constants of backward reactions in equation (4.3) and (4.4). The

initial adsorption of methanol involves dehydrogenation followed by the oxidation of

hydrogen atoms to protons equation (4.3), which react with OH^- ions producing H_2O

molecules. The expression for k_3 is given by (Bard and Faulkner 2001):

$$K_3 = k_3^o \exp\left(\frac{n\alpha F\eta_{a,act}}{RT}\right) \qquad (4.6)$$

Where k_3^o is the standard rate constant, α is the transfer coefficient, which is defined as the

proportion of the electrical energy used for changing the rate of electrochemical reaction

(Equation 4.5). Value of α depends on the nature of the reaction and the electrode material

the value of α ranges between 0 and 1.0 (Larminie and Dicks 2003). n is the number of

electrons transferred during electrooxidation of methanol, which is 4, F is the faraday

constant, T is the temperature and R is universal gas constant. Methanol electrooxidation

reaction order of 0.5 concerning OH^- as well as methanol concentration is given by

Tripkovic et al. (1996). In the present model, the same reaction order concerning methanol

concentration is considered. The corresponding rate equations for equation (4.3) to (4.5) are

given by,

$$r_1 = k_1 C_{CH_3OH} - k_1' \theta_{HCO} \tag{4.7}$$

$$r_2 = k_2 C_{OH}^{0.5} - k_2' \theta_{OH} \tag{4.8}$$

$$r_3 = k_3 \theta_{HCO} \theta_{OH}^{0.5} \tag{4.9}$$

The concentration of methanol and water is represented by C_{CH_3OH} and C_{H_2O} (mol/ml),

respectively. r_1, r_2, and r_3 are the rate of the reactions and θ_i (i = OH, HCHO) is the

factional coverage of the electrode surface. At equilibrium r_1 and r_2 will become zero and

by solving equation (4.7) to (4.9), the rate of reaction for the rate determining step

(Equation 4.9) is given by,

$$r_3 = k_3 K_1 K_2 C_{CH_3OH} C_{OH}^{0.5} \tag{4.10}$$

Where $K_1 = \frac{k_1}{k_1'}$ and $K_2 = \frac{k_2}{k_2'}$ are adsorption desorption equilibrium constants corresponds to

equation (4.3) and (4.4) respectively. Also, the net rate of electrode reaction is governed by

the rate determining step hence it can be expressed as:

$$r_3 = \frac{j}{nF} \tag{4.11}$$

Where j is the current density. On solving equations (4.6), (4.10) and (4.11), the relation

between activation over potential and current density is obtained by,

$$\eta_{a,act,MeoH} = \frac{RT}{\alpha_a nF} \ln \left(\frac{jC_{CH3OH}^{-1} c_{OH}^{-0.5}}{K_{CH3OH}} \right)$$

(4.12)

Where K_{CH_3OH} ($= \eta F k_3^0 K_1 K_2$) is a constant for methanol oxidation. The appropriate values

for k_3^0, K_1, and K_2 needed to be incorporated to estimate K_{CH_3OH}.

4.2.2   Ethanol ($\eta_{a, \, act, \, EtOH}$)

The C-C bond breaking for the complete oxidation of ethanol delays the process of ethanol

electro oxidation. There is no electrocatalyst still developed, which can facilitate complete

ethanol electrooxidation in the range of 30-90 ^{o}C (Lamy et al. 2001). The final product of

partial oxidation of ethanol is acetic acid (Colamati et al. 2006). However, a small quantity

of carbon dioxide is also formed as the final product (Tripkovic et al. 2001 and Tarasevich

et al. 2005). In the present model, it is assumed that the formation of the small quantity of

carbon dioxide can be neglected. The reaction mechanism for ethanol electrooxidation is

similar to that of methanol electrooxidation (Tripkovic et al. 2001). The reaction

mechanism proposed by Tripkovic et al. (2001) is as follows:

$$CH_3CH_2OH \xrightarrow{k_4/k'_4} (CH_3CO)_{ad} + 3H^+ + 3e^-$$

(4.13)

$$\xrightarrow{+3OH^-} 3H_2O$$

$$OH^- \xrightarrow{k_5/k'_5} + (OH)_{ad} + e^-$$

(4.14)

$$(CH_3CO)_{ad} + (OH)_{ad} \xrightarrow{k_6} CH_3COOH$$

(4.15)

Where, k_4, k_5, and k_6 are the rate constants for the forward reactions (Equation 4.13 to 4.15), and k_4' and k_5' are the rate constants for the backward reactions (Equation 4.13 and 4.14). Trasevich et al. (2005) studied the kinetics of ethanol electrooxidation and determined the order of the reaction as 1.0 and 0.7 to 1.0 with respect to ethanol and KOH concentration, respectively. The expression for k_6 is given by Bard and Faulkner (2001).

$$k_6 = k_6^o \exp\left(\frac{n\alpha F \eta_{a,act}}{RT}\right) \tag{4.16}$$

Where k_6^0 is the standard rate constant. The corresponding rate equations for equation (4.13) to (4.15) are given by,

$$r_4 = k_4 C_{EtOH} - k_4' \theta_{CH_3CO} \tag{4.17}$$

$$r_5 = k_5 C_{OH}^{0.5} - k_5' \theta_{OH} \tag{4.18}$$

$$r_6 = k_6 \theta_{CH_3CO} \theta_{OH}^{0.5} \tag{4.19}$$

The concentration of ethanol and water is represented by C_{EtOH} and C_{H_2O} (mol/ml), respectively. r_4, r_5, and r_6 are the rate of the reactions and $\theta_i (i = OH, CH_3CHO)$ is the factional coverage of the electrode surface. At equilibrium r_4 and r_5 will become zero and by solving equations (4.17) to (4.19), the rate of reaction for the rate determining step (Equation 4.19) is given by,

$$r_6 = k_6 K_4 K_5 C_{EtOH} C_{OH}^{0.5} \tag{4.20}$$

Where $K_1 = \frac{k_4}{k'_4}$ and $K_2 = \frac{k_5}{k'_5}$ are adsorption desorption equilibrium constants corresponds to

equation (4.13) and (4.14), respectively. Also, the net rate of electrode reaction is governed

by the rate determining step hence it can be expressed as:

$$r_6 = \frac{j}{nF} \qquad (4.21)$$

Where j is the current density. On solving equations (4.16), (4.20) and (4.21), the relation

between activation over potential and current density is obtained by,

$$(\eta_{a,\ act,\ EtOH}) = \frac{RT}{\alpha_a nF} \ln \left(\frac{jC_{EtOH}^{-1} C_{OH}^{-0.5}}{K_{EtOH}} \right) \qquad (4.22)$$

Where K_{EtOH} $(= \eta F k_6^o K_4 K_5)$ is a lumped parameter for ethanol oxidation. α_a is the charge

transfer coefficient at the anode, and usually, it has a value between 0.1 and 0.5 (Larminie

and Dicks 2003). And j is the current density (mA/cm^2). As ethanol is continuously fed to

the anode side of the microfluidic fuel cell, C_{EtOH} is assumed same as feed concentration of

ethanol.

4.2.3   Sodium Borohydride ($\eta_{a,act,NaBH_4}$)

Morris et al. (1985) reviewed the electrooxidation of the boron compound and quoted that

the oxidation at the anode of BH_4^- in alkaline solution at a platinum electrode occurs

through the ionization of hydrogen from the parent ion (BH_4^-) and from the first hydrolysis

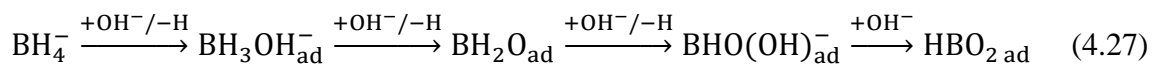product, BH_3OH^-, bound to the electrode surface. They reported that the reaction

mechanism of borohydride is similar to that of methanol and hydrazine. They reported the order of reaction as 1.0 with respect to BH_4^- concentration. The reaction mechanism suggested by Lee et al. (2002) is as follows:

$$BH_4^- \xrightarrow{k_7/k_7'} HBO_{2\,ad} + 5H_2O + 8e^- \qquad (4.23)$$

$$OH^- \xrightarrow{k_8/k_8'} OH_{ad} + e^- \qquad (4.24)$$

$$HBO_{2\,ad} + OH_{ad} + e^- \xrightarrow{k_9} BO_2^- + H_2O \qquad (4.25)$$
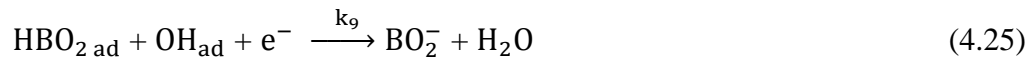
Where, k_7, k_8, and k_9 are rate constants for forwarding reactions in equation (4.23) to (4.25), k_7' and k_8' are rate constants of backward reactions in equation (4.23) and (4.24). The expression for k_9 is given by (Bird and Faulkner 2001)

$$k_9 = k_9^o \exp\left(\frac{n\alpha F\eta_{a,act}}{RT}\right) \qquad (4.26)$$

Where k_9^o is the standard rate constant. Intermediate reaction step for equation (4.23) are:

$$BH_4^- \xrightarrow{+OH^-/-H} BH_3OH_{ad}^- \xrightarrow{+OH^-/-H} BH_2O_{ad} \xrightarrow{+OH^-/-H} BHO(OH)_{ad}^- \xrightarrow{+OH^-} HBO_{2\,ad} \quad (4.27)$$

The order of the reaction with respect to OH^- ion is assumed similar to that of methanol and ethanol. The corresponding rate expressions for equation (4.23) to (4.25) are given below:

$$r_7 = k_7 C_{NaBH_4} - k_7' \theta_{HBO_2} \tag{4.28}$$

$$r_8 = k_8 C_{OH}^{0.5} - k_8' \theta_{OH} \tag{4.29}$$

$$r_9 = k_9 \theta_{HBO_2} \theta_{OH}^{0.5} \tag{4.30}$$

Where C_{NaBH_4} and C_{OH} (mole/ml) are the concentration of sodium borohydride and OH^- ions respectively. Whereas, r_i (i = 7-9) is the rate of reaction and θ_i (i = OH,HBO_2) is the fractional coverage.

At equilibrium reaction rate r_7 and r_8 can be equated to zero and by solving equation (4.28) to (4.30) the rate of the reaction for rate determining step is as follows:

$$r_9 = k_9 K_7 K_8 C_{NaBH_4} C_{OH}^{0.5} \tag{4.31}$$

Where $K_7 = \frac{k_7}{k_7'}$ and $K_8 = \frac{k_8}{k_8'}$ are adsorption desorption equilibrium constants corresponds to equation (4.23) and (4.24), respectively. Also, the net rate of electrode reaction is governed by the rate determining step hence it can be expressed as:

$$r_9 = \frac{j}{nF} \tag{4.32}$$

Where j is the current density.

On solving equation (4.26), (4.31) and (4.32) the relation between activation over potential and current density is given by,

$$(\eta_{a,act,NaBH_4}) = \frac{RT}{\alpha_a nF} \ln \left(\frac{jC_{NaBH_4}^{-1} c_{OH}^{-0.5}}{K_{NaBH_4}} \right) \tag{4.33}$$

Where $K_{NaBH_4} (= \eta F k_9^0 K_7 K_8)$ is a constant for sodium borohydride.

4.3 Ohmic Over potential (η_{ohm})

The voltage drop is the straightforward resistance to the flow of electrons through the material of the electrodes and the various cell interconnections, as well as the resistance to the flow of ions through the electrolyte. This voltage drop is proportional to the current density and is called ohmic losses or sometimes as resistive losses. Ohmic losses are mainly attributed to the electrolyte ionic resistivity ($R_{electrolyte}$) and the external resistance of electrodes and connections ($R_{external}$) where the current is drawn from the cell:

$$\eta_{ohm} = j \, (R_{electrolyte} + R_{external}) \tag{4.34}$$

Ohmic resistance for ionic transport in the channel depends on the average charge transfer distance between the electrodes (d_{ct}), the cross sectional area for charge transfer (A_{ct}), and the ionic conductivity (σ), is denoted by:

$$R_{electrical} = \frac{d_{ct}}{\sigma A_{ct}} \tag{4.35}$$

$$\eta_{ohm} = j \, \left(\frac{d_{ct}}{\sigma A_{ct}} + R_{external} \right) \tag{4.36}$$

The area specific resistances of electrodes, electrode current collecting plate interfaces, and current collectors are denoted by $R_{external}$, which can be measured by a multimeter.

4.4 Concentration Over potential

Concentration overpotential results from the change in concentration of the reactants at the surface of the electrodes as the fuel are used up by the reaction. Concentration affects voltage, and so this type of overpotential is sometimes called concentration loss. In estimating the concentration overpotential, the composite anode and cathode are considered (Fig 4.1 to 4.4).

4.4.1   Anode

The decrease in fuel concentration results in concentration over potential due to the fuel is not replenished immediately at the anode because of mass transfer resistance. One dimensional model is shown in fig (4.1) to (4.2). The electro oxidation of fuel involves two steps (i) transport of fuel from flow channel to electrocatalyst surface, and (ii) electrooxidation of fuel at the electrocatalysts surface. Fuel is continuously supplied to the anode of the microfluidic fuel cell, and thus, the concentration of fuel is assumed constant in the flow channel.

4.4.1.1 Methanol ($\eta_{a,con,MeoH}$)

The fuel concentration in the flow channel is denoted by C_{F,CH_3OH} (mol/ml) and the electrocatalyst layer is denoted by C_{S,CH_3OH} (mol/ml).

The methanol transportation from flow channel to electrocatalyst layer is described by,

$$N^d_{CH_3OH} = k_f(C_{F,CH_3OH} - C_{S,CH_3OH}) \tag{4.37}$$

Where $N^d_{CH_3OH}$ is denoted as the flux through diffusion layer for methanol and k_f is the mass transfer coefficient. The mass transfer coefficient from the feed stream to the diffusion layer is approximately expressed by using the empirical equation (Jeng et al., 2002):

$$k_f = 1.87 \times 10^{-4} \left(\frac{j}{0.003}\right)^{0.32} \tag{4.38}$$
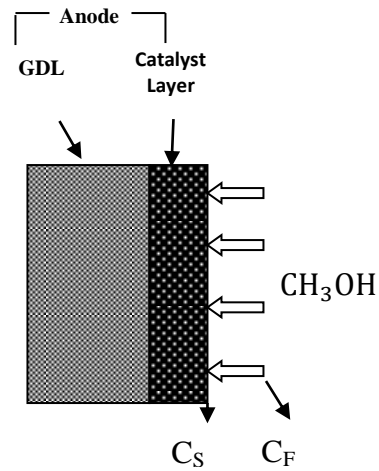
Figure 4.1 Schematic presentation of methanol transportation at the anode.

The methanol electrooxidation takes place on the electrocatalyst layer of the anode and thus, is written as,

$$N^d_{CH_3OH} = -\frac{j}{nF} \tag{4.39}$$

The diffusion layer is made of a porous carbon substrate, which is inactive to the electrochemical reaction in the microfluidic fuel cell. As the cell is exposed to the atmosphere so, the pressure has been assumed constant, i.e., 1 atm at both anode and cathode. Water is partially consumed in electrooxidation of fuel at anode electrocatalyst layer, and the remaining water is transported through the flow stream. Combining the equation (4.37) and (4.39) the following expression is obtained,

$$- \frac{j}{nF} = k_f (C_{F,CH_3OH} - C_{S,CH_3OH}) \tag{4.40}$$

From equation (4.40):

$$C_{S,CH_3OH} = \frac{j}{nFk_f} + C_{F,CH_3OH} \tag{4.41}$$

The rate of electrochemical reaction of methanol is written using modified Butler-Volmer equation (Colmati et al. 2006).

$$j = j_0 \frac{C_{S,CH_3OH}}{C_{F,CH_3OH}} \exp \left(\frac{\alpha_a nF \eta_{a,con}}{RT} \right) \tag{4.42}$$

Where, j_0 is the exchange current density in (mA/cm^2). By solving equation (4.41) and (4.42), eliminating C_{S,CH_3OH} the model equation for anode concentration over potential is obtained as,

$$(\eta_{a,con,MeoH}) = \frac{RT}{nF\alpha_a}\ln\left(\frac{j}{j_o[j/\eta Fk_fC_{F,CH_3OH}+1]}\right)$$

(4.43)

4.4.1.2 Ethanol ($\eta_{a,con,EtOH}$)

The transport process of ethanol from bulk to electrocatalyst surface is similar to methanol fuel, as described in fig (4.2). The fuel concentration in the flow channel is denoted by C_{F,CH_3OH} (mol/ml) and the electrocatalyst layer is denoted by C_{S,CH_3OH} (mol/ml).

The Ethanol transportation from flow channel to electrocatalyst layer is described by,

$$N^d_{EtOH} = k_f(C_{F,EtOH} - C_{S,EtOH})$$

(4.44)

Where N^d_{EtOH} and is the flux for ethanol and k_f is the mass transfer coefficient.
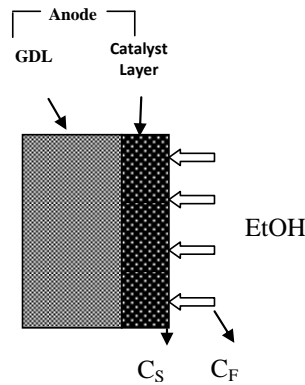
Figure 4.2 Schematic of ethanol transportation at the anode.

The mass transfer coefficient from the feed stream to the diffusion layer is approximately expressed by the empirical equation (Jeng et al. 2002):

$$k_f = 1.87 \times 10^{-4} \left(\frac{j}{0.003}\right)^{0.32} \tag{4.45}$$

The fuel electrooxidation takes place on the electrocatalyst layer of the anode and thus is written as,

$$N_{EtOH}^d = -\frac{j}{nF} \tag{4.46}$$

Combining the equation (4.44) and (4.46) the following expression is obtained,

$$-\frac{j}{nF} = k_f \left(C_{F,EtOH} - C_{S,EtOH}\right) \tag{4.47}$$

From equation (4.47):

$$C_{S,EtOH} = \frac{j}{nFk_f} + C_{F,EtOH} \tag{4.48}$$

The rate of electrochemical reaction of Ethanol is written using modified Butler-Volmer equation (Colmati et al. 2006),

$$j = j_0 \frac{C_{S,EtOH}}{C_{F,EtOH}} \exp\left(\frac{\alpha_a nF\eta_{a,con}}{RT}\right) \tag{4.49}$$

Where, j_0 is the exchange current density (mA/cm^2). By solving equation (4.48) and (4.49),

eliminating $C_{S,EtOH}$, the model equation for anode concentration over potential is obtained as,

$$\eta_{a,con,EtOH} = \frac{RT}{nF\alpha_a}\ln\left(\frac{j}{j_o[j/\eta Fk_f C_{F,EtOH}+1]}\right) \tag{4.50}$$

4.4.1.3 Sodium borohydride ($\eta_{a,con,NaBH_4}$)

The fuel concentration in the flow channel is denoted by $C_{F,NaBH_4}$ (mol/ml) and the electrocatalyst layer is denoted by $C_{S,NaBH_4}$. The sodium borohydride transportation from flow channel to electrocatalyst layer is described by,

$$N_{NaBH_4}^d = k_f(C_{F,NaBH_4} - C_{S,NaBH_4}) \tag{4.51}$$

Where $N_{NaBH_4}^d$ is denoted as the flux of sodium borohydride and k_f is the mass transfer coefficient.
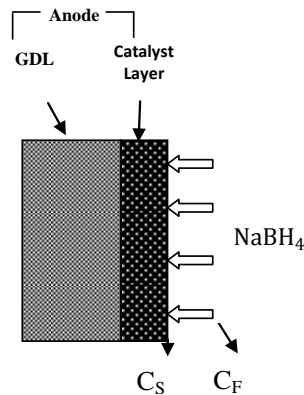
Figure 4.3 Schematic of sodium borohydride transportation at the anode.

The mass transfer coefficient from the feed stream to the diffusion layer is approximately expressed by the empirical equation (Jeng et al. 2002):

$$k_f = 1.87 \times 10^{-4} \left(\frac{j}{0.003}\right)^{0.32} \tag{4.52}$$

The fuel electro oxidation takes place on the electrocatalyst layer of the anode and thus is written as,

$$N_{NaBH_4}^d = -\frac{j}{nF} \tag{4.53}$$

Combining the equation (4.51) and (4.53) the following expression is obtained,

$$-\frac{j}{nF} = k_f \left(C_{F,NaBH_4} - C_{S,NaBH_4}\right) \tag{4.54}$$

From equation (4.54)

$$C_{S,NaBH_4} = \frac{j}{nFk_f} + C_{F,NaBH_4} \tag{4.55}$$

The rate of electrochemical reaction of sodium borohydride as fuel is written using modified Butler-Volmer equation (Colmati et al. 2006),

$$j = j_0 \frac{C_{S,NaBH_4}}{C_{F,NaBH_4}} \exp\left(\frac{\alpha_a nF\eta_{a,con}}{RT}\right) \tag{4.56}$$

Where, j_0 is the exchange current density (mA/cm^2) at anode. By solving equation (4.55) and (4.56), eliminating $C_{S,NaBH_4}$ the model equation for anode concentration over potential is obtained as,

$$\eta_{a,con,NaBH_4} = \frac{RT}{nF\alpha_a} \ln \left(\frac{j}{j_o[j/\eta Fk_f C_{F,NaBH_4} + 1]} \right) \qquad (4.57)$$

4.4.2   Cathode

It is known that reaction kinetics of oxygen on Pt based cathode in alkaline medium is excellent. The current drawn from the microfluidic fuel cell depends on the extent of decrease in partial pressure of oxygen. The concentration or partial of oxygen at the electrocatalyst surface becomes very low at high current density. The decrease in partial pressure of oxygen results in concentration over potential as oxygen will not be replenished at the cathode because of mass transfer resistance. As described in literature review chapter (page no. 41). The electroreduction of oxygen in an alkaline medium generally proceeds by one or two pathways (Ortiz et al. 2003). The direct oxygen reduction to OH^- ions, i.e., single electron pathway is described below:

$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \qquad (4.58)$$

Or an oxygen reduction to HO_2^- ions, i.e., two electron pathway:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \qquad (4.59)$$
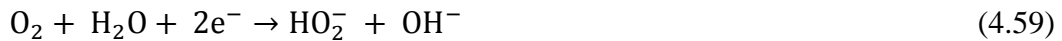
With subsequent reduction of peroxide ions to OH^- ions, i.e., two electron pathway

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \tag{4.60}$$

Equations (4.59) and (4.60) are collectively produce $2 + 2$ electron mechanism (Ortiz et al. 2003).

One dimensional cathode model similar to that of the anode is considered fig (4.4). Oxygen diffuses through the carbon paper (diffusion layer) to reach the cathode electrocatalyst layer, where ORR takes place. It is assumed that the concentration of oxygen at the interface of air and carbon paper is C_{ob} and the concentration of oxygen tin the electrocatalyst layer is C_{oc}. Under steady state condition and by species conservation, the oxygen molar flux, N_{O_2}, is related to the current density, j, as,

$$N_{O_2} = \frac{j}{nF} \tag{4.61}$$

One dimensional Fick's law regarding the molar flux of oxygen is used to describe the transport of oxygen in the carbon paper it is given by,

$$N_{O_2} = -D_{O_2}^{d,eff} \frac{(C_{oc} - C_{ob})}{l_d} \tag{4.62}$$

Where, $D_{O_2}^{d,eff}$ is the effective diffusivity of oxygen in porous media with the porosity of ε^d. $D_{O_2}^{d,eff}$ is evaluated from the bulk diffusivity, Do_2, using Bruggeman's expression (Jeng et al. 2004):

$$D_{O_2}^{d,eff} = \varepsilon^{d(3/2)} D_{O_2} \tag{4.63}$$

The diffusion coefficient for oxygen, D_{O_2} at different cathode temperatures and 1 bar pressure is determined by the following correlation (Srinivasan et al. 1992).

$$D_{O_2} = 2.88 \times 10^{-6} \exp\left[2933\left(\frac{1}{313} - \frac{1}{T}\right)\right] \tag{4.64}$$

Where, temperature (T) is in ^{o}K. The rate of oxygen reduction reaction is described using modified Butler-Volmer equation (Bard et al. 2001) and simplified in terms of oxygen concentration at the electrocatalyst layer as,

$$j = j_0 \frac{C_{oc}}{C_{ob}} \exp\left(\frac{\alpha_c nF\eta_{c,conc}}{RT}\right) \tag{4.65}$$

Where α_c is the transfer coefficient, and j_0 is the exchange current density at the cathode. The exchange current density at the anode and cathode is assumed to be same (Martinez-Baca et al. 2004). The value of n depends on the stoichiometry of oxygen reduction reaction, and it is equal to 4 (Equation 4.56). On solving equation (4.57) to (4.60), the expression for concentration over potential is derived as,

$$\eta_{c,conc} = \frac{RT}{nF\alpha_c} \ln\left(\frac{j}{j_0[1-jM]}\right) \tag{4.66}$$

Where M is a constant defined as,

$$M = \frac{l_d C_{ob}}{nF\varepsilon^{d\left(\frac{3}{2}\right)} D_{O_2}}$$ (4.67)
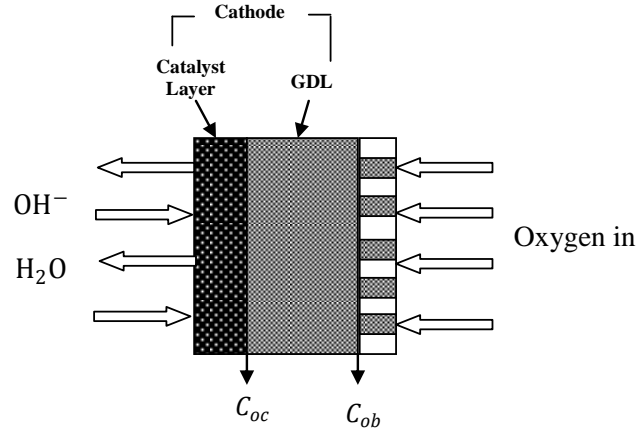
Figure 4.4 Schematic of O_2 transport through the cathode.

4.5 Model Equation

4.5.1   Methanol

The final reaction of methanol as a fuel is generated by adding two half-cell reactions at the anode (Equation 4.3 to 4.5) and cathode (Equation 4.58) which is given by:

$$CH_3OH + O_2 \rightarrow HCOOH + H_2O$$ (4.68)

The over potentials, η, is defined as the deviation of cell voltage, E_{cell}, from the open circuit voltage. The E_{cell} can be calculated from the following equation:

$$E_{cell} = E{-}\eta = E - (\eta_{act} + \eta_{ohm} + \eta_{con})$$ (4.69)

By incorporating the expression for activation, ohmic and concentrations over potentials in equation (4.69), the final model equation is given below:

$$E_{cell} = E - \frac{RT}{\alpha_a NF} \ln \left(\frac{jC_{CH3OH}^{-1} c_{OH}^{-0.5}}{K_{CH3OH}} \right) - j \left(\frac{d_{ct}}{\sigma A_{ct}} + R_{external} \right) - \frac{RT}{nF\alpha_a} \ln \left(\frac{j}{j_o[j/\eta Fk_f C_{F,CH_3OH} + 1]} \right) - \frac{RT}{nF\alpha_c} \ln$$

$$\left(\frac{j}{j_o[1-jM]} \right) \tag{4.70}$$

4.5.2 Ethanol

The final reaction of ethanol as a fuel is generated by adding two half-cell reactions at the anode (Equation 4.13 to 4.15) which is given by:

$$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O \tag{4.71}$$

The overpotentials, η, is defined as the deviation of cell voltage, E_{cell}, from the open circuit voltage. The E_{cell} can be calculated from the following equation:

$$E_{cell} = E\text{-}\eta = E - (\eta_{act} + \eta_{ohm} + \eta_{con}) \tag{4.72}$$

By incorporating the expression for activation, ohmic and concentrations overpotentials in equation (4.72), the final model equation is given below:

$$E_{cell} = E - \frac{RT}{\alpha_a nF} \ln \left(\frac{jC_{EtOH}^{-1} c_{OH}^{-0.5}}{K_{EtOH}} \right) - j \left(\frac{d_{ct}}{\sigma A_{ct}} + R_{external} \right) - \frac{RT}{nF\alpha_a} \ln \left(\frac{j}{j_o[j/\eta Fk_f C_{F,EtOH} + 1]} \right) - \frac{RT}{nF\alpha_c} \ln \left(\frac{j}{j_o[1-jM]} \right)$$

$$\tag{4.73}$$

4.5.3   Sodium borohydride

The final reaction of sodium borohydride as fuel is generated by adding two half-cell reactions at the anode (Equation 4.23 to 4.25) which is given by:

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O \tag{4.74}$$

The overpotentials, η, is defined as the deviation of cell voltage, E_{cell}, from the open circuit voltage. The E_{cell} can be calculated from the following equation:

$$E_{cell} = E\text{-}\eta = E - (\eta_{act} + \eta_{ohm} + \eta_{con}) \tag{4.75}$$

By incorporating the expression for activation, ohmic and concentrations over potentials in equation (4.75), the final model equation is obtained as given below:

$$E_{cell} = E - \frac{RT}{\alpha_a NF}\ln\left(\frac{jC_{NaBH_4}^{-1}c_{OH}^{-0.5}}{K_{NaBH_4}}\right) - j\left(\frac{d_{ct}}{\sigma A_{ct}} + R_{external}\right) - \frac{RT}{nF\alpha_a}\ln\left(\frac{j}{j_o[j/\eta Fk_fC_{F,NaBH_4} + 1]}\right) - \frac{RT}{nF\alpha_c}\ln$$

$$\left(\frac{j}{j_o[1-jM]}\right) \tag{4.76}$$

From the above equations, one can determine operating voltage and current density of the microfluidic fuel cell for a given load of the different operation parameters and constants are known.