

Theoretical mathematical modeling and computer simulation of direct methanol fuel cell (DMFC)

* Abdulkareem A.S¹⁾, Jimoh, A²⁾, Afolabi A.S³⁾ Muzenda E⁴⁾ and Oyesegun O.R⁵⁾

1), 2), 5) Department of Chemical Engineering, School of Engineering and Engineering Technology, Federal University of Technology, PMB 65 Gidan Kwano, Minna Niger State Nigeria

3) Department of Civil and Chemical Engineering, College of Science, Engineering and Technology. University of South Africa P/Bag X6, Florida 1710 Johannesburg South Africa

4) Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Johannesburg South Africa

1)kasaka2003@futminna.edu.ng

ABSTRACT

The depletion in petroleum resources and environmental concerns has lead to a movement towards an environmentally friendlier and more efficient power production sources for a more stable world. Fuel cell technologies, especially Direct Methanol Fuel Cell (DMFC) is considered as highly promising and environmental friendly alternative energy source for different applications. This study is concerned with an investigation of effects of temperature, pressure and concentration on the DMFC performance using a mathematical model and simulation of the developed model with a computer programme (JAVA).The results obtained reveals that the cell voltage decreased by approximately 0.0001volts as the temperature was increased by 10K and the current density also increases significantly, and the cell voltage increased by approximately 0.001volts as the pressure was increased by 1bar. Also increase in concentration by 0.5M results in reduction of output voltage by 0.0001volts at different current densities. The results obtained from the simulation of the model equation also reveals that increment in operating temperature by 10K leads to about 20KJ increase in the heat generated by the system and change in operating pressure and concentration of the cell has no observable influence on the heat generated by the cell. It can be inferred from the simulated results that the cell performance and efficiency are reduced by increase in temperature and concentration, while an increment in pressure improves the cell performance. Temperature has observable influence on the heat generated by the fuel cell but pressure and concentration have no effect. Hence, the result of the of the numerical simulation clarifies the influence of the operating conditions on the performance and efficiency of DMFC

1. INTRODUCTION

Fossil fuel is the world's most popular energy source and it is presently becoming scarcer due to overdependence on it as a source of energy for both industrial and domestic consumption. Apart from over dependence on fossil fuel, world's energy reserve are also limited, the situation that led to energy crisis and price instability (Abdulkareem et al, 2012). Apart from the problems of fossil fuel highlighted above, health, political and environmental issues are also major factors contributing to energy crisis with environmental impacts of fossil as a major concern (Yilanci *et al.*, 2008). For instance burning of fossil fuel products for energy generation releases toxic waste that pollutes the air. Hence the products of combustion of fossil fuels contribute immensely to climate change (Davis, 2000). Energy crisis is now going from bad to worse especially in developing countries where there is no action plan to fight the problem of overdependence on the fossil fuel (Abdulkareem et al., 2012). Series of efforts have been put in place by researchers and government agencies to prevent future damage of environment as a result of over dependence on fossil fuel for energy generation, these efforts led to development of ecologically friendly methods of generating energy (Yilanci *et al.*, 2008). These methods include tidal, hydrodynamic, wind, solar and geothermal, though these alternative methods of energy production is environmentally friendly, however the quantities of energy generated by these methods are small to meet up with the energy demand and also need specific environment to performed effectively. The recent research and development in the area of alternative energy is focusing on the development of alternative energy that can compete well with the existing energy in terms of availability and burning efficiency. In this respect, fuel cell technology is considered as the perfect way to energy sources that can compete well with the fossil fuels in terms of availability and efficiency without producing any pollutants (Abdulkareem, 2010). Presently, proton exchange membrane fuel cell (PEMFC), Direct methanol fuel cell (DMFC), Solid oxide fuel cell (SOFC), Alkali fuel cell (AFC), Phosphoric oxide fuel cell (POFC) and Solid oxide fuel cell (SOFC) are the commercially available fuel cell. The focus of this study is on the development of theoretical mathematical modeling for direct methanol fuel cell (Hansan *et al.*, 2006; Nice and Strickland, 2011).

Direct methanol fuel cell (DMFC) is a class of fuel cell that utilizes proton exchange membrane as electrolyte with methanol as the fuel. Higher energy densities of DMFC gives it advantages over batteries for portable applications. The drawbacks of DMFC are the crossover of fuel and oxidation of the fuel at the anode side (Dohle *et al.*, 2002; Kulikovsky, 2003; Sandhu et al, 2005; Chen et al, 2006). Despite the advantages of fuel cell as a perfect alternative energy source, the technology is not commercially available due to lack of understanding of the interaction of various parameters and how it affects the performance of the cell. In this study, the development of a predictive model and computer simulation of direct methanol fuel cell will be reported. The developed model will be use to study the effect of various parameters such as concentration of fuel (methanol), operating temperature and operating pressure of the

fuel cell. The model will also be used to simulate the influence of these parameters on the heat generated from the cell and efficiency of the fuel cells based on the operating conditions. ...

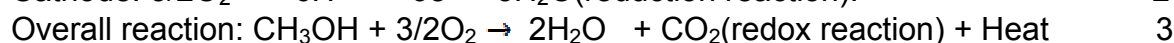
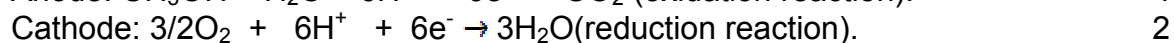
2. CONCEPTUALIZATION OF THE MODELING TECHNIQUE

Direct Methanol Fuel Cell (DMFC) which is described as a device that converts chemical energy into electrical energy is a promising power source that depends on the membrane and the electro-catalyst (Ge and Liu, 2005; Thomassin et al, 2006; Hansan *et al.*, 2006). The major problems of the DMFC is the methanol cross over which depresses cathode performance and reduce the fuel efficiency, this problem can be solve through development of new catalyst (Afolabi et al, 2012). Also affecting the performance and commercial availability of DMFC is the lack of proper understanding of influence of operating parameters on the cell performance. Hence, the need to study the contributing effects of operating parameters on the cell performance through mathematical model which is the focus of this study. In this study, the effects of different parameters such as pressure, temperature and fuel concentration on the performance of DMFC will be investigated through the simulation of mathematical models. The following assumptions were made during conceptualization of the model:

1. The heat loss in the system is by radiation, natural convection and forced convection.
2. The enthalpy calculation for each inputs and outputs of the cell was based on the standard temperature of 298K.
3. Activation, ohmic and concentration losses were encountered in the cell.
4. The outlet temperature of both the fuel and oxidant is equal to that of the cell stack.
5. Net heat is assumed equal to heat accumulation.

2.1 ELECTROCHEMICAL MODEL

Activation polarization is a product of the energy activity in fuel cell which involves the formation and breaking of bonds at the electrodes is shown in Equations 1-3. During the electro chemical reaction of direct methanol fuel cells (Equations1-3), heat, water and electricity are generated (Shukla et al, 2002)



The total net output voltage from the fuel cell is (Abdulkareem et al., 2013)

$$V_{(l)} = V_{rev} - V_{irrev} \quad 4$$

where V_{rev} = reversible cell voltage, V_{irrev} = over potential that occurred in the cell.

The reversible cell voltage for a DMFC is ideally described by the Nernst equation as follows (Yilanci *et al.*, 2008):

$$V_{rev} = E_0 + \frac{RT}{nF} \{(\ln(P\text{CH}_3\text{OH}) + 3/2\ln(P\text{O}_2) - (2\ln(P\text{H}_2\text{O}) + \ln(P\text{CO}_2))\} \quad 5$$

Equation 5 can be rewritten as:

$$V_{rev} = E_O + \frac{RT}{nF} \ln\left\{\frac{P_{CH_3OH} \cdot (P_{O_2})^{1.5}}{P_{CO_2} \cdot (P_{H_2O})^2}\right\} \quad 6$$

where;

P_{CH_3OH} = Partial pressure of methanol available at the anode (bar).

P_{H_2O} = Partial pressure of water at the cathode which is 1 when liquid water is produced (bar).

P_{O_2} = Partial pressure of oxygen at the cathode (bar).

R = Universal gas constant (8.314 J/mol K).

E_O = potential of the methanol and oxygen reaction (volts).

F = Faraday's constant (94,485 c/mol).

n = number of electrons.

$$E_O = \frac{\Delta G_{rxn}}{nF} \quad 7$$

where ΔG_{rxn} = energy of the reaction (joules).

Irreversible voltage loss consists of the activation over potential or loss, ohmic over potential or loss and concentration or diffusion over potential or loss. Irreversible voltage can be expressed as:

$$V_{irrev} = V_{act} + V_{conc} + V_{ohmic} \quad 8$$

where;

V_{act} = Activation over potential or loss (volts).

V_{conc} = Concentration over potential or loss (volts).

V_{ohmic} = ohmic over potential or loss (volts).

Activation loss which occurs at both the anode and the cathode, it is related by the Bolter-Volmer as shown in Equation 9 (Munoz de Escalona *et al.*, 2011):

$$V_{act} = \frac{RT}{nF\alpha_a} \cdot \ln\left(\frac{i}{i_o}\right) + \frac{RT}{nF\alpha_c} \ln\left(\frac{i}{i_o}\right) \quad 9$$

where; i = current density.

The term current density (i) in Equation 9 can be evaluated using the relationship shown in Equation 10 (Sousa *et al.*, 2010):

$$i = i_{oa} \exp\left(\frac{\alpha_a nF}{RT} \cdot (E_O - E_{eq})\right) - i_{oc} \exp\left(\frac{-\alpha_c nF}{RT} \cdot (E_O - E_{eq})\right) \quad 10$$

The anode and cathode current density can be evaluated from the relationship shown in Equations 11 and 12 respectively (Sousa *et al.*, 2010):

$$i_a = i_{oa} \exp\left[\frac{\alpha_a nF}{RT} \cdot (E_O - E_{eq})\right] \quad 11$$

$$i_c = i_{oc} \exp\left[-\frac{\alpha_c nF}{RT} \cdot (E_O - E_{eq})\right] \quad 12$$

where;

α_a = anodic transfer coefficient in the cell.

α_c = cathodic transfer coefficient in the cell.

i_{oa} and i_{oc} = exchange current density at the anode and cathode respectively (A/cm²)

Ohmic loss (V_{ohmic}) occurs due to electrical losses in the cell. Miansari et al (2009) suggested that ohmic loss can be evaluated from the relationship shown in Equation 13

$$V_{ohmic} = \gamma \exp\left(\beta\left(\frac{1}{T_{FC}} - \frac{1}{T_{ref}}\right)\right) iR^{internal} \quad 13$$

where, γ = constant coefficient at the fuel cell (0.2 ohms), β = constant coefficient at the fuel cell (-2870K), $R^{internal}$ = internal resistance of the cell, T_{FC} = cell operating temperature, T_{ref} = reference temperature of the fuel cell.

Similarly, concentration losses occur, which is the consequence of mass transfer of reactants and products resistance through the porous electrode can be evaluated from relationship shown in Equation 14 (Brouwer *et al.*, 2006).

$$V_{conc} = \frac{RT}{nF} \cdot \ln(1 - i/j_l) \quad 14$$

Where,

$$j_l = 2 \cdot F \cdot K_H \cdot C_{rxn} \quad 15$$

j_l = limiting current density (A/cm²), K_H = mass transfer coefficient; C_{rxn} = concentration at the reactant (mol/cm³).

Substituting Equations 6, 9, 13 and 14 into Equation 4 yield;

$$V_{(i)} = E_o + \frac{RT}{nF} \cdot \ln\left\{\left(\frac{i}{i_o}\right)^{\frac{1}{\alpha_a}} \cdot \left(\frac{i}{i_o}\right)^{\frac{1}{\alpha_c}} \cdot \left[\frac{1 - i_{total}}{j_l}\right] \cdot \frac{p_{H_2O}^2}{(P_{CH_3OH} \cdot P_{O_2}^{1.5})}\right\} \gamma \exp\left[\beta\left(\frac{1}{T_{FC}} - \frac{1}{T_{ref}}\right)\right] \quad 16$$

Equation 16 is the predictive model for the voltage output from DMFC as a function of operating parameters such as operating temperature, anodic pressure, cathodic pressure and concentration of the fuel (methanol).

2.2 MASS BALANCE OF THE DMFC

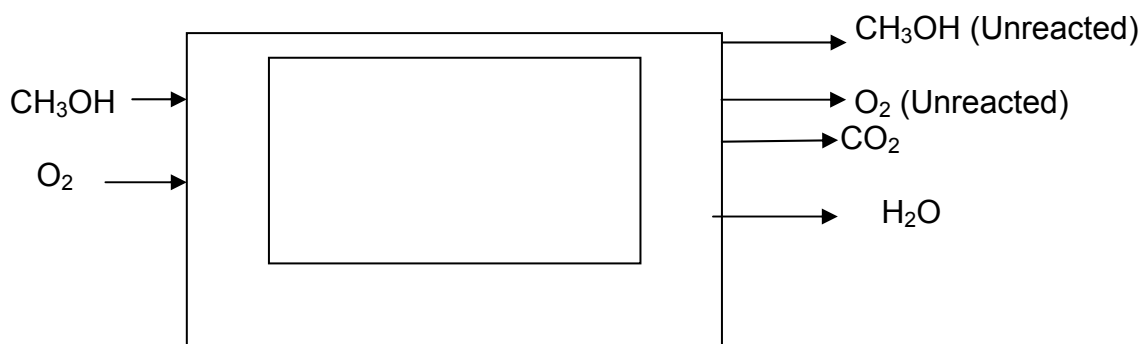


Fig1: Schematic of material flow in DMFC.

Figure 1 represents the flow of the fuel (methanol), oxidant (oxygen) and products of

electro chemical reaction in and out of the cell. The mass balance of the cell has to be considered for proper account of the masses of the reactants in and out of the system based on Faraday's law (Dincer *et al.*, 2008).

$$\text{Input} = \text{output} + \text{accumulation} \quad 17$$

$$m_{CH_3OH,in} = m_{CH_3OH,react} + m_{CH_3OH,out} \quad 18$$

$$m_{O_2,in} = m_{O_2,react} + m_{O_2,out} \quad 19$$

where $m_{CH_3OH,in}$ and $m_{O_2,in}$ = mass flow rates of methanol and oxygen into the system respectively, $m_{CH_3OH,out}$ and $m_{O_2,out}$ = mass flow rates of methanol and oxygen leaving the cell (unreacted methanol and oxygen) . Some basic principles of electrochemistry will be used to calculate the rate at which methanol and oxygen reacted in the cell, $m_{CH_3OH,react}$ and $m_{O_2,react}$, and also the rate of production of water and CO₂ that is, $m_{H_2O,out}$ and m_{CO_2} which are functions of current density and Faraday's constant.

The rate of consumption of methanol is given as (Yilanci *et al.*, 2008):

$$m_{CH_3OH,react} = \zeta_A M_{CH_3OH} * \frac{i_{AFC}}{nF} * 10^{-3} \quad 20$$

Similarly, the reaction of oxygen occurs at the cathode, therefore the rate of consumption of oxygen is given as (Yilanci *et al.*,2008):

$$m_{O_2,react} = \zeta_C M_{O_2} * \frac{i_{AFC}}{nF} * 10^{-3} \quad 21$$

where, ζ_A and ζ_C stands for the anode and cathode stoichiometry respectively, M_{CH_3OH} and M_{O_2} are the molecular weight of methanol and oxygen respectively, i is the current density, A is the area of the fuel cell, n is number of moles and F is Faraday's constant (Yilanci *et al.*,2008).

Dincer *et al* (2008) shows that the rate of production of water from electro chemical reaction at the anode and cathode is:

$$m_{H_2O,out} = M_{H_2O} * \frac{i_{AFC}}{nF} * 10^{-3} \quad 22$$

Similarly the rate of production of CO₂ from electro chemical reaction which occurs at the anode is;

$$m_{CO_2} = M_{CO_2} * \frac{i_{AFC}}{nF} * 10^{-3} \quad 23$$

where, M_{H_2O} and M_{CO_2} are the molecular weights of water and co₂ respectively.

From Equations 18 and 19, the rate of methanol and oxygen leaving the system unreacted can be evaluated as follows:

$$\text{since , } m_{CH_3OH,in} = m_{CH_3OH,react} + m_{CH_3OH,out}$$

Therefore,

$$m_{CH_3OH,out} = m_{CH_3OH,in} - m_{CH_3OH,react} \quad 24$$

$$m_{CH_3OH,out} = m_{CH_3OH,in} - \zeta_A M_{CH_3OH} * \frac{i_{AFC}}{nF} * 10^{-3} \quad 25$$

Also since, $m_{O_2,in} = m_{O_2,react} + m_{O_2,out}$

Therefore,

$$m_{O_2,out} = m_{O_2,in} - m_{O_2,react} \quad 26$$

$$m_{O_2,out} = m_{O_2,in} - \zeta_C M_{O_2} * \frac{i_{AFC}}{nF} * 10^{-3} \quad 27$$

2.3 ENERGY BALANCE OF DMFC

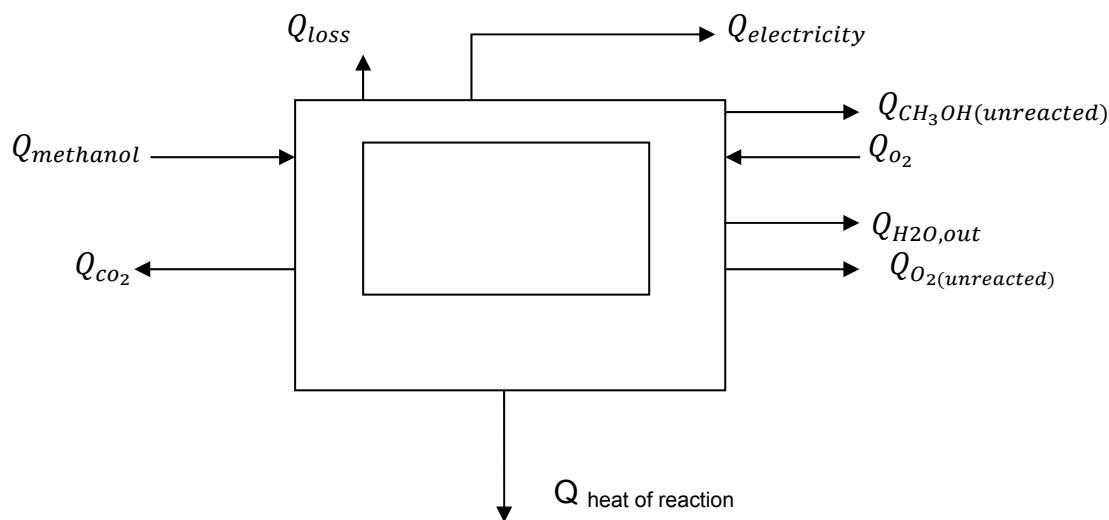


Fig 2: Schematic of heat (energy) flow in DMFC.

The energy balance of the fuel cell can be said to be the inflow of heat of the reactants entering the system which is equal to the outflow of heat of the products leaving the system and accumulation that occurred within the system, which can be represented mathematically as:

$$Energy\ input - Energy\ output - Accumulation = 0 \quad 28$$

$$Q_{input} - Q_{output} - Q_{net} = 0 \quad 29$$

From assumption number 5 i.e. heat accumulation is assumed equal to the net heat generated by the cell i.e.

$$Q_{net} = Q_{accumulation}$$

$$Q_{net} = Q_{input} - Q_{output} \quad 30$$

$$Q_{input} = Q_{methanol} + Q_{oxygen} \quad 31$$

$$Q_{output} = Q_{CO_2} + Q_{loss} + Q_{methanol(unreacted)} + Q_{H_2O} + Q_{O_2(unreacted)} + Q_{reaction} \quad 32$$

$$Q_{loss} = Q_{convection} + Q_{radiation} \quad 33$$

$$Q_{convection} = Q_{natural\ convection} + Q_{forced\ convection} \quad 34$$

Substitute Equation 34 into Equation 33 to obtain;

$$Q_{loss} = Q_{nc} + Q_{Fc} + Q_{rad} \quad 35$$

$$Q_{nc} = h_{nc}A(T_F - T_0) \quad 36$$

$$Q_{Fc} = m_{coolant} C_{p,air} (T_{coolant,out} - T_0) \quad 37$$

$$Q_{rad} = \varepsilon\sigma A(T_F^4 - T_0^4) \quad 38$$

where; A =heat transfer area of the fuel cell in cm², h_{nc} = natural convective heat transfer coefficient(W/m²K) ,T₀ =ambient temperature (assumed to be 298K), m_{coolant} = coolant air flow rate, T_{coolant,out} =outlet temperature of the coolant air leaving the fuel cell stack in kelvin,ε = surface emissivity, which is the fraction of radiated energy emitted(0 < ε < 1), σ is Stefan-Boltzmann constant(5.67x10⁻⁸ W/m²K⁴) (Yilanci *et al.*,2008).

$$Q_{methanol} = m_{methanol,in} \int_{T_{in}}^{T_F} C_p dT \quad 39$$

$$Q_{O_2} = m_{O_2,in} \int_{T_{in}}^{T_F} C_p dT \quad 40$$

$$Q_{CO_2} = m_{CO_2} \int_{T_F}^{T_{out}} C_p dT \quad 41$$

$$Q_{electricity} = VIT \quad 42$$

$$Q_{methanol(unreacted)} = m_{methanol,out} \int_{T_F}^{T_{out}} C_p dT \quad 43$$

$$Q_{H_2O,out} = m_{H_2O,out} \int_{T_F}^{T_{out}} C_p dT \quad 44$$

$$Q_{O_2,unreacted} = m_{O_2,out} \int_{T_F}^{T_{out}} C_p dT \quad 45$$

Since, $Q_{net} = Q_{input} - Q_{output}$, then

$$Q_{net} = Q_{methanol,in} + Q_{O_2,in} - (Q_{CO_2} + Q_{loss} + Q_{electricity} + Q_{methanol(out)} + Q_{H_2O,out} + Q_{reaction}) \quad 46$$

Substituting Q_{loss} and $Q_{electricity}$, into Equation 46 to obtain;

$$Q_{net} = Q_{methanol,in} + Q_{O_2,in} - (Q_{CO_2} + h_{nc}A(T_F - T_0) + m_{coolant} C_{p,air} (T_{coolant,out} - T_0) + \varepsilon\sigma A(T_F^4 - T_0^4) + VIT + Q_{methanol(out)} + Q_{H_2O,out} + Q_{O_2(out)} + Q_{reaction}.) \quad 47$$

Abdulkareem et al (2013) suggest that for a mechanically reversible and closed processes system $Q = \Delta H$, which is the molar or specific enthalpy of a system. Equation 47 can therefore write in terms of ΔH ;

$$Q_{net} = \Delta H_{methanol,in} + \Delta H_{O_2,in} - (\Delta H_{CO_2} + h_{nc}A(T_F - T_0) + m_{coolant} C_{p,air} (T_{coolant,out} - T_0) + \varepsilon\sigma A(T_F^4 - T_0^4) + VIT + \Delta H_{methanol(out)} + \Delta H_{H_2O,out} + \Delta H_{O_2(out)} + \Delta H_{reaction.}) \quad 48$$

T_0 = reference temperature which is 298K (25°C), T_F =operating temperature of the cell. $\Delta H = mR \int_{T_0}^{T_F} \frac{C_P}{R} dT = m \int_{T_0}^{T_F} C_P dT$, to evaluate the equation of the integral, the knowledge of the temperature dependence of the heat capacity is required. This is given by the following empirical equation shown in Equation 49 (Smith *et al.*, 2005):

$$\frac{C_P}{R} = \alpha + \beta T + \gamma T^2 \quad \text{or} \quad C_P = \alpha + \beta T + \gamma T^2 \quad 49$$

where α, β and γ are constants characteristics of a particular substance.

The enthalpy of the material in and out of the direct methanol fuel can be evaluated as shown below.

2.3.1 ENTHALPY OF METHANOL

Methanol is inputted into the system at temperature 298K which is also the reference temperature and it being heated to a temperature, T_F which is the fuel cell temperature. Therefore the heat of formation of methanol at 298K will be considered in computing the enthalpy.

$$\Delta H_{methanol,in} = m_{methanol,in} \int_{298}^{T_F} C_P dT \quad 50$$

$$\Delta H_{methanol,in} = m_{methanol,in} [\Delta H^o_{f,methanol,298k} + \int_{298}^{T_F} (\alpha + \beta T + \gamma T^2 + \delta T^3)] \quad 51$$

Integrate Equation 51 to obtain;

$$\Delta H_{methanol,in} = m_{methanol,in} \left[\Delta H^o_{f,methanol,298k} + \left(\alpha(T - 298) + \beta \frac{(T^2 - 298^2)}{2} + \gamma \frac{(T^3 - 298^3)}{3} + \frac{(T^4 - 298^4)}{4} \right) \right] \quad 52$$

Similarly, the enthalpy of methanol out or unreacted, $\Delta H_{methanol(out)}$, which is the heat of methanol leaving the cell unreacted. Since the methanol leaves the cell at the temperature of the fuel cell, it can be calculated as thus:

$$\Delta H_{methanol(out)} = \Delta H_{methanol,in} - \Delta H_{methanol,react} \quad 53$$

$$\Delta H_{methanol(out)} = m_{methanol,in} \left[\Delta H^o_{f,methanol,298k} + \left\{ \alpha(T - 298) + \beta \frac{(T^2 - 298^2)}{2} + \right. \right.$$

$$\gamma \left\{ \frac{(T^3-298^3)}{3} + \delta \frac{(T^4-298^4)}{4} \right\} - \zeta_A M_{CH_3OH} * \frac{i_{AFC}}{nF} * 10^{-3} \left[\Delta H^o_{f\text{methanol},298k} + \left\{ \alpha(T-298) + \beta \frac{(T^2-298^2)}{2} + \frac{(T^3-298^3)}{3} \right\} \right] \quad 54$$

Rearrange Equation 54 to obtain;

$$\Delta H_{\text{methanol}(out)} = m_{\text{methanol},in} - \zeta_A M_{CH_3OH} * \frac{i_{AFC}}{nF} * 10^{-3} \left[\Delta H^o_{f\text{methanol},298k} + \left\{ \alpha(T-298) + \beta \frac{(T^2-298^2)}{2} + \gamma \frac{(T^3-298^3)}{3} + \delta \frac{(T^4-298^4)}{4} \right\} \right] \quad 55$$

2.3.2 ENTHALPY OF OXYGEN

Oxygen enters the cell at the temperature of 298K which is also the reference temperature and is being heated to a temperature, T_F of the fuel cell. Since the heat of formation of oxygen is zero because oxygen is an element, the enthalpy of oxygen input will be:

$$\Delta H_{O_2,in} = m_{O_2,in} \int_{298}^{T_F} C_P dT \quad 56$$

$$\Delta H_{O_2,in} = m_{O_2,in} \int_{298}^{T_F} (\alpha + \beta T + \gamma T^2 + \delta T^3) \quad 57$$

$$\Delta H_{O_2,in} = m_{O_2,in} \left\{ \alpha(T-298) + \beta \frac{(T^2-298^2)}{2} + \gamma \frac{(T^3-298^3)}{3} + \delta \frac{(T^4-298^4)}{4} \right\} \quad 58$$

where $\Delta H_{O_2,in}$ is the enthalpy of oxygen input from the reference temperature, 298K to the temperature of the cell.

In a similar manner, the enthalpy of oxygen out is

$$\Delta H_{O_2(out)} = \Delta H_{O_2,in} - \Delta H_{O_2,react} \quad 59$$

$$\Delta H_{O_2(out)} = m_{O_2,in} \int_{298}^{T_F} C_P dT - \zeta_C M_{O_2} * \frac{i_{AFC}}{nF} * 10^{-3} \int_{298}^{T_F} C_P dT \quad 60$$

$$\Delta H_{O_2(out)} = m_{O_2,in} \left\{ \alpha(T-298) + \beta \frac{(T^2-298^2)}{2} + \gamma \frac{(T^3-298^3)}{3} + \delta \frac{(T^4-298^4)}{4} \right\} - \zeta_C M_{O_2} * \frac{i_{AFC}}{nF} * \left\{ \alpha(T-298) + \beta \frac{(T^2-298^2)}{2} + \gamma \frac{(T^3-298^3)}{3} + \delta \frac{(T^4-298^4)}{4} \right\} \quad 61$$

Equation 61 can be re arrange to obtain,

$$\Delta H_{O_2(out)} = m_{O_2,in} - \zeta_C M_{O_2} * \frac{i_{AFC}}{nF} * 10^{-3} \left\{ \alpha(T-298) + \beta \frac{(T^2-298^2)}{2} + \gamma \frac{(T^3-298^3)}{3} + \delta \frac{(T^4-298^4)}{4} \right\} \quad 62$$

2.3.3 ENTHALPY OF WATER PRODUCED

Water is produced at the cathode of the cell at a temperature of T_F of the cell, it leaves the cell at that same temperature. This can be evaluated as follows:

$$\Delta H_{H_2O,out} = \Delta H_{fH_2O,T_F} + \int_T^{T_F} C_P dT \quad 63$$

$T=T_F$, therefore

$$\Delta H_{H_2O,out} = \Delta H_{fH_2O,T_F} = m_{H_2O,out} (\Delta H_{fH_2O,298} + \int_{298}^{T_F} C_P dT) \quad 64$$

$$\Delta H_{H_2O,out} = m_{H_2O,out} \left\{ (\Delta H_{fH_2O,298} + \int_{298}^{T_F} (\alpha + \beta T + \gamma T^2 + \delta T^3) dT) \right\} \quad 65$$

Integrate Equation 65 to obtain;

$$\Delta H_{H_2O,out} = M_{H_2O} * \frac{iA_{FC}}{nF} * 10^{-3} \left[\Delta H_{fH_2O,298k}^o + \left\{ \alpha(T - 298) + \beta \frac{(T^2 - 298^2)}{2} + \gamma \frac{(T^3 - 298^3)}{3} + \delta \frac{(T^4 - 298^4)}{4} \right\} \right] \quad 66$$

2.3.4 ENTHALPY OF CO₂ PRODUCED, ΔH_{CO_2}

$$\Delta H_{CO_2} = \Delta H_{fCO_2,T_F} + \int_T^{T_F} C_P dT \quad 67$$

T=T_F, therefore

$$\Delta H_{CO_2} = \Delta H_{fCO_2,T_F} = m_{CO_2} (\Delta H_{fCO_2,298} + \int_{298}^{T_F} C_P dT) \quad 68$$

$$\Delta H_{CO_2} = m_{CO_2,out} \left\{ (\Delta H_{fCO_2,298} + \int_{298}^{T_F} (\alpha + \beta T + \gamma T^2 + \delta T^3) dT) \right\} \quad 69$$

Upon integration,

$$\Delta H_{CO_2} = M_{CO_2} * \frac{iA_{FC}}{nF} * 10^{-3} \left[\Delta H_{fCO_2,298k}^o + \left\{ \alpha(T - 298) + \beta \frac{(T^2 - 298^2)}{2} + \gamma \frac{(T^3 - 298^3)}{3} + \delta \frac{(T^4 - 298^4)}{4} \right\} \right] \quad 70$$

2.3.5 ENTHALPY OF REACTION

The heat of reaction is the enthalpy change when the number of moles of methanol and oxygen in their standard state at temperature of the fuel cell react to form a certain number of moles of water and CO₂ in their standard state at the same temperature of the fuel cell.

The fundamental equation relating heats of reaction to temperature is given as (Smith *et al.*, 2005):

$$\Delta H_{rxn} = \Delta H_{rxn}^o + R \int_{298}^{T_F} \frac{\Delta C_P}{R} dT \quad \text{OR} \quad \Delta H_{rxn} = \Delta H_{rxn}^o + \int_{298}^{T_F} \Delta C_P dT \quad 71$$

where ΔH_{rxn} and ΔH_{rxn}^o are heats of reaction at temperature T_F of the fuel cell and at reference temperature 298K.

$$\Delta C_P = \left\{ (1 * C_{PCO_2}) + (2 * C_{PH_2O}) \right\} products - \left\{ (1 * C_{PCH_3OH}) + (3/2 * C_{PO_2}) \right\} reactants \quad 72$$

$$\Delta H_{rxn} = \Delta H_{rxn,298}^o + \int_{298}^{T_F} (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2 + \Delta\delta T^3) dT \quad 73$$

Upon integration,

$$\Delta H_{rxn} = \Delta H_{rxn,298}^o + \left\{ \Delta\alpha \cdot (T - 298) + \Delta\beta \cdot \frac{(T^2 - 298^2)}{2} + \Delta\gamma \cdot \frac{(T^3 - 298^3)}{3} + \Delta\delta \cdot \frac{(T^4 - 298^4)}{4} \right\} \quad 74$$

$$\Delta H_{rxn,298}^o = (n_i \Delta H_{fi}^o)_{products} - (n_i \Delta H_{fi}^o)_{reactants} \quad 75$$

where

$$\Delta\alpha = (\alpha_{CO_2} + 2\alpha_{H_2O}) - (\alpha_{CH_3OH} + \alpha_{O_2})$$

$$\Delta\beta = (\beta_{CO_2} + 2\beta_{H_2O}) - (\beta_{CH_3OH} + \beta_{O_2})$$

$$\Delta\gamma = (\gamma_{CO_2} + 2\gamma_{H_2O}) - (\gamma_{CH_3OH} + \gamma_{O_2})$$

$$\Delta\delta = (\delta_{CO_2} + 2\delta_{H_2O}) - (\delta_{CH_3OH} + \delta_{O_2})$$

where, n_i is the number of moles of each product and reactant that is their stoichiometry ratio, and ΔH_{fi}^o is the standard enthalpy or heat of formation of both the reactants and products. The reaction in direct methanol fuel cell is:



That is 1 mole of methanol and $\frac{3}{2}$ moles of oxygen produced 1 mole of CO_2 and 2 moles of H_2O .

$$\Delta H_{rxn,298}^o = \{(1 * \Delta H_{fCO_2}^o) + (2 * \Delta H_{fH_2O}^o)\}products - \{(1 * \Delta H_{fCH_3OH}^o) + (\frac{3}{2} * \Delta H_{fO_2}^o)\}reactants \quad 77$$

2.4 EFFICIENCY

DMFC efficiency can be evaluated from relationship shown in Equation 78

$$\eta_{cell} = \frac{V_{cell}}{E^o} \quad 78$$

In reality, the electrochemical reaction that produces energy in fuel cell system cannot achieve 100% conversion (Haynes, 2001; Qi et al, 2005). Certain fraction of the reactant will flow out of the system as shown in Fig.2. It is therefore, important to consider fuel utilization while computing the fuel cell efficiency. Abdulkareem (2010) define fuel cell utilization as;

$$\delta_f = \frac{\text{Mass of fuel (methanol) reacted in the cell}}{\text{Mass of fuel (methanol) unreacted in the cell}} \quad 79$$

Equation 78 then becomes;

$$\eta_{cell} = \delta_f \frac{V_{cell}}{E^o} \quad 80$$

3. RESULTS AND DISCUSSION

Despite the compelling advantages of the DMFCs as alternative energy sources, the technology is still lack behind due to the lack of proper understanding of the influence of operating parameters on the cell performance of the cell. This study is focused on the development of a theoretical mathematical model that can be use to predict the performance of a DMFC. For the purpose of estimating cell performance as a function of operating parameters, a parametric model was developed and the model developed was simulated using java. Empirical thermodynamic modeling equations and energy analysis equations were evaluated as function of the cell operating conditions to investigate the effects of the operating parameters on the output voltage of the cell and the efficiency of the system. The results obtained are presented in Figures 3-12. Presented in Figure 3 is the simulated results obtained on the influence of temperature on the cell performance at different current densities, with operating pressure of 1 bar and methanol concentration of 0.25 Mol/cm^3 . The simulated results obtained as presented indicate that voltage output is decreasing with increase in current density. For instance at operating of temperature 343k and current density 100 mA/cm^2 , the voltage output was 0.9497volts when the current density was raised to 400 mA/cm^2 , the

cell voltage reduces to 0.9496 volts. Results as presented also shown that rise in cell temperature led to reduction in cell voltage output. The inverse proportionality of the temperature effect on the cell performance can be blame on the possibility of the fuel (methanol) cross in the cell as the temperature increases. This pattern of results obtained agrees with the results obtained by Miansari *et al* (2009) in their experimental studies.

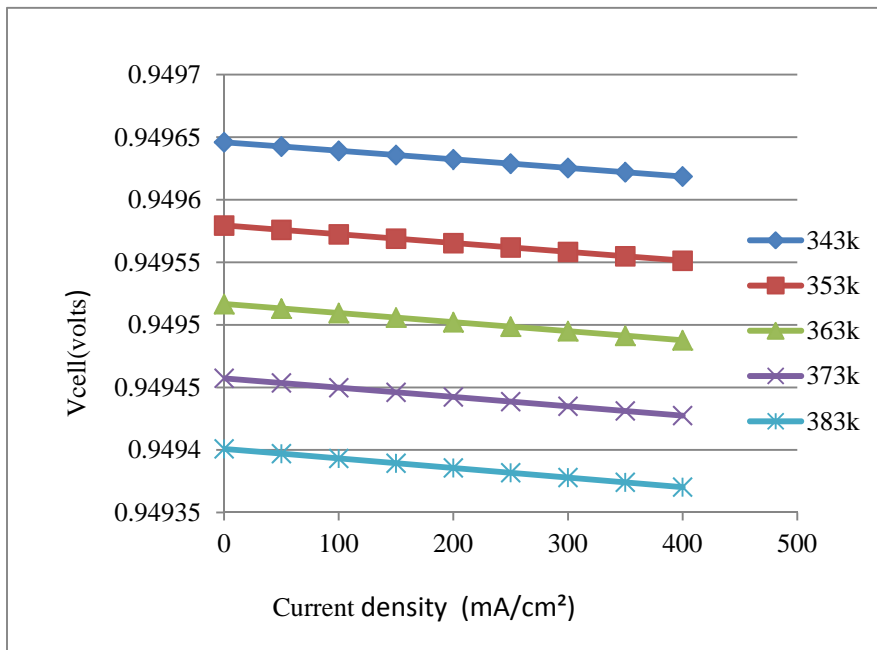


Fig 3: Influence of temperature on the voltage output of DMFC.

Also simulated is the influence of oxygen pressure on the performance of the DMFC and the results obtained are presented in Fig.4. Results obtained indicate that operating pressure of the cathode also referred to as oxygen pressure positively affects the cell performance. For instance, at cathode operating pressure of 1.5bar and current density of 100mA/cm², the voltage output of 0.957volts was obtained, and when the pressure was raised to 2.5bar, at same current density of 100mA/cm², the output voltage of 0.9582volts was obtained. The positive influence of cathode operating pressure on the DMFC performance can be attributed to the reduction in methanol cross over. Also simulated is the effect of anode pressure (operating pressure of methanol) on the performance of DMFC and the results obtained are presented in Fig.5. This effect was simulated at constant temperature of 343K, while the anode pressure was varied between 1 to 2.5 bar. Results obtained also indicate that operating pressure of the cell positively affect the DMFC performance. For instance, at anode operating pressure of 1bar and current density of 150mA/cm², the simulated output voltage obtained was 0.9403volts, as the pressure increase to 2.5bar, at same current density of 150mA/cm², the simulated voltage output also increases to

0.9411volts. This pattern of results is in agreement with earlier results reported by Yan and Tien-Chien (2008). These results indicate that an increase in pressure increases the output voltage of the cell. In summary simulated results indicate that operating pressure of the anode and cathode positively affects the performance of DMFC.

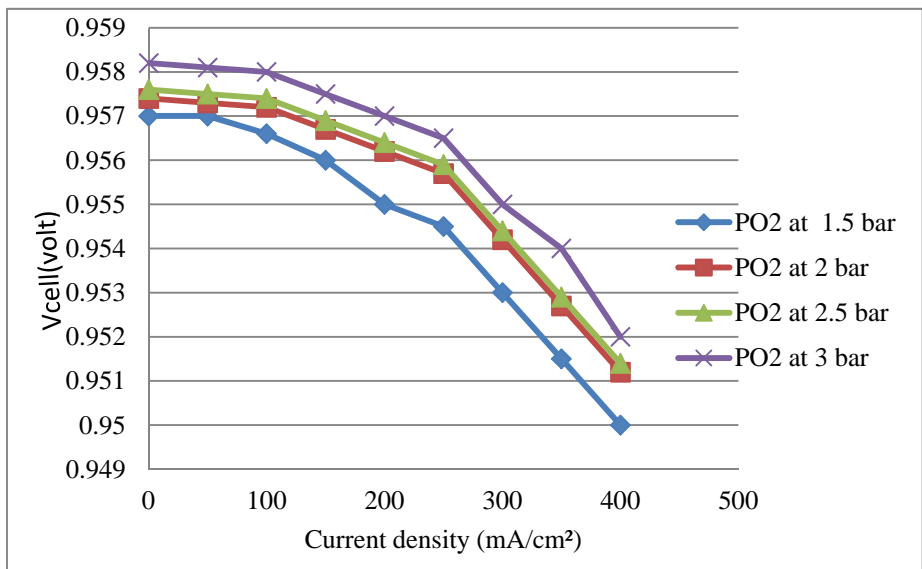


Fig 4: Influence of cathode pressure on the voltage output of DMFC.

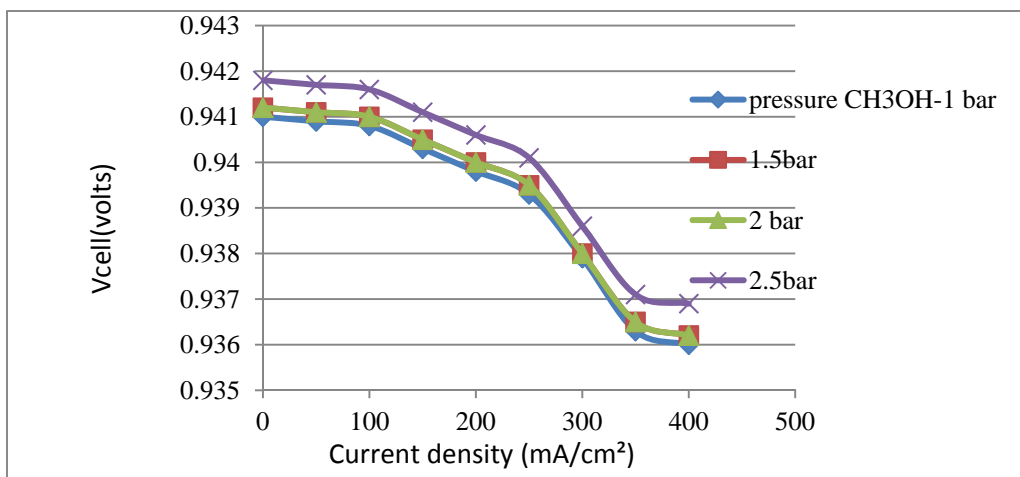


Fig 5: Influence of anode pressure on the voltage output of DMFC.

Depicted in Fig.6 is the simulated results obtained on the effects of fuel (methanol) concentration on the performance of DMFC. Results obtained as presented indicate that fuel (methanol) concentration of 0.5M and current density of 200mA/cm² will give voltage output of 0.9379volts. When the fuel (methanol) concentration was raised to 2M under same condition of current density the voltage output from the cell reduces to

0.9372volts. This can be blame on the fact that at lower methanol concentration, the rate of methanol cross over will be minimal, it is however worth of mentioning that cell operate at lower methanol concentration might not sustain high current densities operation because of the initiation of limiting current operation(ref). Results obtained conform to the pattern of results reported by Yan and Tien-Chien (2008).

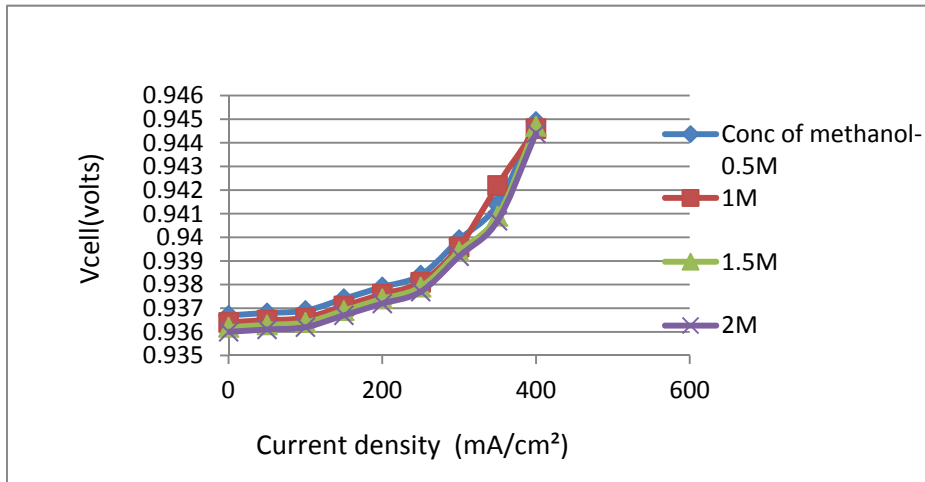


Fig 6: Influence of fuel (methanol) concentration on DMFC performance.

Presented in Fig 7 is the simulated results obtained on the influence of temperature on the cell efficiency. Simulated results obtained as presented reveal increase in temperature negatively affects the efficiency of the cell. For instance at operating temperature of temperature 343K, and current density 100mA/cm², an efficiency of 77.019% was obtained, as the operating temperature increases to 383K, the cell efficiency reduces to 76.99% . These results agreed with the results reported by Miansari et al (2009). Though, efficiency of the direct methanol fuel cell should be increase with rise in operating temperature, however the thermal stability of the membrane militates against operating the cell at high temperature. The consequence of reduction in thermal stability of the membrane at high temperature leads to low electro-activity of the methanol oxidation at the anode side of the electrode. This resulted into large volume of undesired fuel (methanol) to be move through the membrane from anode to the cathode side which resulted into low efficiency of the cell at high operating temperature.

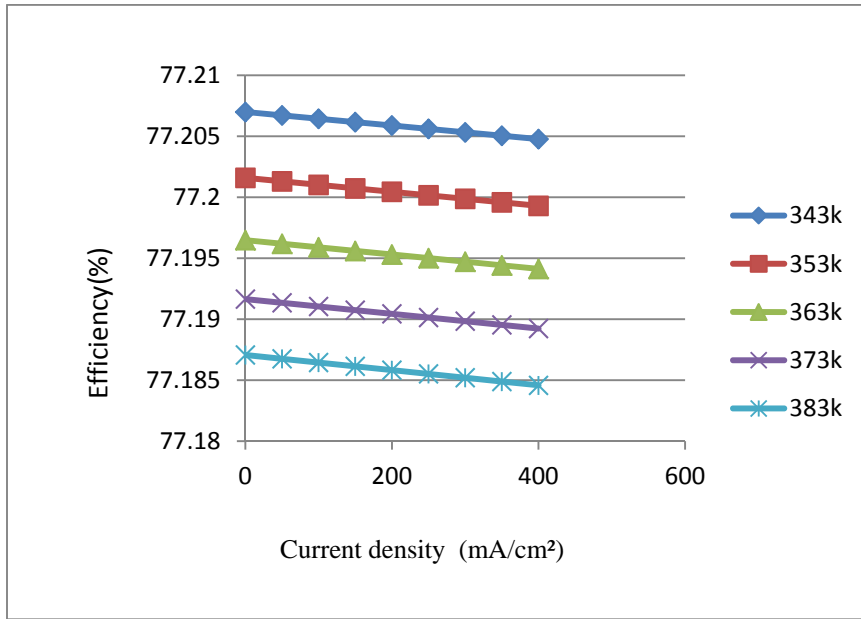


Fig 7: Effect of operating temperature on the efficiency of direct methanol fuel cell temperatures.

The by-product of electrochemical reaction that takes place in the cell of DMFC is heat. However, the waste heat from cells can be harnessed for the purpose of improving the cell efficiency. Ability of the cell to capture the heat generated for use in a co-generation like manner necessitates the need to evaluate the quantity of heat produced by the cell. Results obtained on the influence of operating temperature on the net heat generated by the cell are presented in Fig 8. Results as presented indicate that operating temperature has a positive influence on the heat generated by the cell. For instance at operating temperature of 343K, the simulated net heat generated was approximately 110kJ, when the operating temperature increases to 383K, the net heat generated becomes approximately 215kJ. Though, the results obtained indicate that increasing the operating temperature favour the net heat generated by the cell, care must be taken not increase the operating temperature beyond the limit that the membrane can withstand.

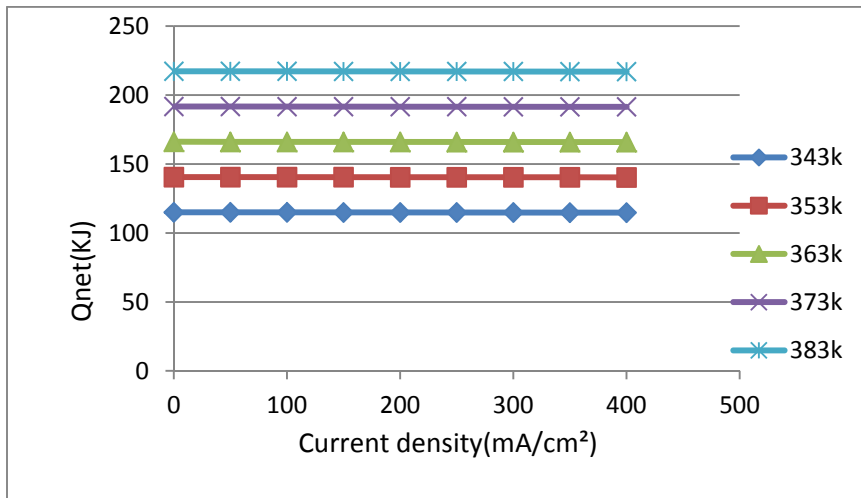


Fig. 8: Effect of operating temperature on heat generation by the direct methanol fuel cell.

CONCLUSIONS

This present study is intended to develop a predictive mathematical model for the performance of DMFC at various operating conditions. To achieve this, electrochemical and energy analysis was carried out and the model developed was simulated with computer programme (java). From the model result, a general conclusion can be drawn that the fuel cell performance can be improved significantly by adopting any or a combination of the different operating parameters. The following specific conclusions can be drawn from this study based on the simulated results obtained;

(1) Operating temperature negatively influence the performance and efficiency of direct methanol fuel cell, due to strong methanol flux across the membrane which resulted into cathode potential. However, operating temperature positively affects the net heat generated by the cell, which implies that net heat generated in the cell increase with increase in temperature.

(2) Simulation of the developed model also shows that increase in the pressure of the fuel cell will increase the performance of the cell and increase the current density. This shows that the efficiency of the cell increases with an increase in pressure.

(3) The model also demonstrates that a high methanol feed concentration leads to a strong methanol crossover through the membrane and thus reduces the cell voltage and efficiency. However the model also tells us that an increase in the methanol concentration can be valuable to the system as it increases the current density of the cell.

Acknowledgements

University Board of Research (UBR), Federal University of Technology Minna, Nigeria is highly appreciated for their support. STEPB project of Federal University of

Technology, Minna, Nigeria is also appreciated for their support. Support received from University of Johannesburg and University of South Africa (UNISA) is also appreciated.

REFERENCES

- Abdulkareem A. S, Afolabi A. S, Idibe C. A, Pienaar .H.C.vZ and Iyuke S. E. (2013) "A predictive model for energy analysis of proton exchange membrane fuel cell by computer simulation". *J. of Energy Sources Part A*: **35**(1), 32 – 41.
- Abdulkareem A.S (2010) "Design and Development of proton exchange membrane from synthetic rubber and Carbon nanoballs for proton exchange membrane fuel cell". PhD Thesis, University of the Witwatersrand, Johannesburg, South Africa (unpublished).
- Abdulkareem A.S, Abdulfatai J, Afolabi A.S, Odigure J.O and Patience D. (2012) "Production and characterization of biodiesel from non-edible oils: An alternative energy source to petrol diesel". *Energy Conservation*.
- Alexandre Hacquard.(2005). "Improving and Understanding Direct Methanol Fuel Cell Performance", Unpublished M.SC thesis. Worcester polytechnic institute, USA.
- Brouwer. J, Jabbari. F, Leal. E.M and Orr. T .(2006) "Analysis of a molten carbonate fuel cell: Numerical modeling and experimental validation". *J. of Power Sources*, **158**, 213-224.
- Chen. W, Sun. G, Guo. J, Zhao. X, Yan. S, Tian. J, Tang. S, Zhou. Z and Xin. Q (2006) "Test on the degradation of direct methanol fuel cell". *Electrochimica Acta*, **51**, 239-2399.
- Dohle, H., Divisek, J., Merggel, J., Oetjen, H. F., Zingler, C., and Stolten, D.(2002). "Recent Developments of the Measurement of the Methanol Permeation in a Direct Methanol Fuel Cell", *J. of Power Sources* **105**(2), 274-282.
- Ge. X, Huang. X, Zhang. Y, Lu. Z, Yu. J, Chen. K, Dung. D, Liu. Z, Miao. J and Su. W. (2006) "Screen-printed thin YSZ films used as electrolytes for solid oxide fuel cells". *J. of Power Sources*, **59**, 1048–1050.
- Hansan Liu, Chaojie Song, Lei Zhang, Jiujun Zhang, Haijiang Wang, David P. Wilkinson. (2006). "A review of anode catalysis in the direct methanol fuel cell", *J. of Power Sources* **155**(23), 95-110
- Haynes. C .(2001): "Clarifying reversible efficiency misconceptions of high temperature fuel cells in relation to reversible heat engines". *J. of Power Sources*, **92**, 199-203.
- Kulikovsky. A. A .(2003) "Analytical model of the anode side of DMFC: the effect of non-Tafel kinetics on cell performance". *Electrochemistry Communications*, **5**, 530-538.
- Miansari Me., Sedighi, K., Amidpour, M., Alizadeh, E. and Miansari, Mo.(2009). "Experimental and thermodynamic approach on proton exchange membrane fuel cell performance", *J. of Power Sources*, **190**, 356-361.
- Munoz de Escalona,J.M., Sanchez, D., Chacartegui,R., Sanchez, T.(2011). "A step-by-step methodology to construct a model of performance of molten carbonate fuel cells with internal reforming", *Int.J.Hydrogen Energy* ,**36**,15739-15751.

- Nice, Karim and Strickland, Jonathan.(2011)."How Fuel Cells Work: Polymer Exchange Membrane Fuel Cells", New York, pp.47-88.
- Qi. Y, Huang. B, Chuang. K.T. (2005) "Dynamic modeling of solid oxide fuel cell: The effect of diffusion and inherent impedance". *J. of Power Sources*, **150**, 32 – 47.
- Sandhu. S.S, Crowther. R.O and Fellnerb. J.P .(2005) "Prediction of methanol and water fluxes through a direct methanol fuel cell polymer electrolyte membrane". *Electrochimica Acta*, **50**, 3985-3991.
- Scott. K, Argyropoulos. P and Sundmacher. K .(1999) "A model for the liquid feed direct methanol fuel cell". *J. of Electroanalytical Chemistry*, **477**, 97-110.
- Shukla. A.K, Jackson. C.L, Scott. K and Raman. R.K .(2002) "An improved-performance liquid-feed solid-polymer-electrolyte direct methanol fuel cell operating at near-ambient conditions". *Electrochimica Acta*, **47**, 3401-3407.
- Sousa, T., Mamlouk, M. and Scott, K.(2010). "An isothermal model of a laboratory intermediate temperature fuel cell using PBI doped phosphoric acid membranes", *Chemical Engineering Science*,**65**,2513-2530.
- Thomassin . J-M, Pagnouille. C, Caldarella. G , Germain. A and Jérôme. R .(2006) "Contribution of nanoclays to the barrier properties of a model proton exchange membrane for fuel cell application". *J.of Membrane Science*, **270**. Pp 50–56.
- Xu. T (2005) "Ion exchange membranes: State of their development and perspective". *J.of Membrane Science (Review)*, **263**. Pp 1-29.
- Yan,T.Z. and Tien-Chien Jen.(2008). "Two-phase flow modeling of liquid-feed direct methanol fuel cell", *Int. J of Heat and Mass Transfer*, **51**, 1192-1204.
- Yilanci, A., Dincer, I. and Ozturk, H.K. (2008) "Performance analysis of a PEM fuel cell in a solar-hydrogen system", *Int.J. Hydrogen Energy*, **33**,7538-7552.