

Predictive mathematical modeling and Computer Simulation of Direct Ethanol Fuel Cell

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Keywords:	Fue cell, Direct ethanol fuel cell, Predictive mathematical modelling, Simulation, Operation parameters

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Predictive mathematical modeling and Computer Simulation of Direct Ethanol Fuel Cell

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Abstract

The challenges of finding a better substitute of energy as well as the short comings identify with direct ethanol fuel cell, this includes; high anode over potential and crossover necessitate the need to investigate the influence operating parameters on the performance of fuel through computer simulation. This study focus on the development of a predictive mathematical modeling for direct ethanol fuel cell for the purpose of investigating the influence pressure, temperature cathode and reactants concentration on the performance, efficiency and heat generated by the cell. Results obtained indicate that increase in operating temperature resulted led to decrement in output voltage and cell efficiency, while same condition of increasing the temperature positively favour the heat generated from the cell. Simulated results also show that cell performance is improved with increase in concentration of the fuel (ethanol) and oxidant (oxygen). It can be inferred from this study that the cell performance of DEFC can be theoretically predicted with the developed model.

Keyword: Fuel cell, direct ethanol fuel cell, predictive mathematical modeling, simulation and operation parameters

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1. Introduction

Geometric rise in the global economic development, technology improvement and population increases are the major factors identified responsible for in balancing of the fossil fuel supply and demand (Sanchez and Cardona, 2008; Balat and Balat, 2009; Abdulkareem et al., 2012).

It has been reported that the consequence of fossil fuel demand outgrowing supply generated price instability, which led to what is now known as energy crises. Literature also revealed that the lesson learnt from energy crises of 1970, was the realization that fossil fuel apart from the price instability, there is also a problems of environmental pollution that are associated with the utilization of fossil for energy generation (Suresh and Jayanti, 2011). Fossil fuels are non-renewable resources and take millions of years to form, it has been reported that fossil fuel reserves are being depleted faster than its rate of generation (Hussain et al., 2005; Abdulkareem et al., 2010; Suresh and Jayanti, 2011).

The problem of energy crises and environment impacts that are associated with combustion of fossil fuel necessitate the need for alternative means of generating energy sources which is the fossil fuel (Xianguo, 2006; Inoue et al, 2006; Suresh and Jayanti, 2011). Fuel cells had been suggested as a much feasible alternative energy source that can replace fossil fuel because they are free from undesirable emissions which are common to fossil fuel. Cleanliness, efficiency and envisaged effectiveness of adequate power supply also favoured the choice of fuel cell as a sustainable alternative energy (Souzy et al, 2005; Bai et al, 2006; Ha et al, 2006). Among the various types of fuel cells presently available, DEFC is seen as the most promising and sustainable one. Non toxicity, non polluting renewability and high power densities are the attribute of DMFC (Schlake et al, 2006; Chen et al, 2006). Despite the realization that fuel cell will serve as a perfect solution to energy problems, the technology is still not available in commercial quantities due to monopolies of technology and lack of proper understanding of interaction between the various parameters that influence the

performance of fuel cell. In this study, predictive mathematical model will be derived for the purpose of determining the performance of direct ethanol fuel cell at different operating parameters.

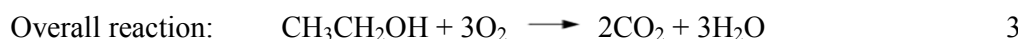
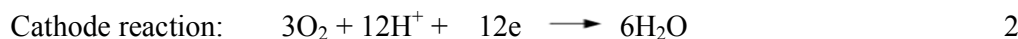
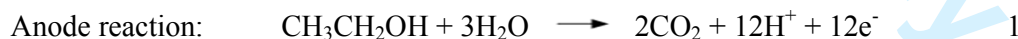
2. Development of the predictive model

For the purpose of achieving the commercial availability of fuel cell, particularly DEFC, there is the need to study the interaction of operating parameters that influence output voltage and efficiency of DEFC which is the focus of this study. Assumptions made for the development of the model are;

(1) The cell operates initially at standard condition of temperature and pressure at both anode and cathode ends respectively (2) The effect of catalyst poison during operation is neglected, while the membrane electrolyte is fully humidified (3). Activation loss, Ohmic loss and Concentration loss are the losses (over potential) encountered in the proton exchange membrane fuel cell fuelled with ethanol (4) Heat loss in the system is by natural convection, force convection and radiation. Heat accumulation is also assumed equal to the net heat generated by the cell.

2.1 Electrochemical model

The electrochemical behaviour of a DEFC can be represented by reactions shown in Equations 1-3 (Andreadis et al., 2006)



Tsiakara et al (2006) shown in their work that the output voltage of the cell can be evaluated from the relationship shown in Equation 4;

$$V_{\text{cell}} = V_{\text{rev}} - V_{\text{irrev}} \quad 4$$

Where, $V_{\text{rev}} = E_{\text{equ}}$ represent thermodynamic equilibrium cell potential and varies with molar concentration of the oxidized and reduced reactants, it is given by the Nernst equation presented in Equation 4 (Larminie and Dicks, 2001).

$$E_{\text{equ}} = E^{\circ} - \frac{RT}{nF} \ln [P_{(\text{H}_2\text{O})}^3 \cdot P_{(\text{CO}_2)}^2 / P_{(\text{EtOH})} \cdot P_{(\text{O}_2)}^3] \quad 5$$

Where E° = standard cell potential, R =ideal gas constant (8.314 j/molK), T = absolute temperature (K), n = number of moles of electrons, F =faraday's constant (96500 C/mol).

From Equation 4, the term V_{irrev} which is the summation of loss in the cell can be evaluated from the relationship shown in Equation 6 (Abdulkareem et al, 2010)

$$V_{\text{irrev}} = V_{\text{act}} + V_{\text{conc}} + V_{\text{ohmic}} \quad 6$$

From Equation 6, the activation voltage loss (V_{act}) which is the consequence of the slowness of the electrochemical reactions that takes place on the electrodes is expressed as (Andreadris and Tsiakaras, 2006);

$$V_{\text{act}} = \frac{RT}{nF\alpha_a} \ln \left\{ \frac{i}{i_0} \right\} + \frac{RT}{nF\alpha_b} \ln \left\{ \frac{i}{i_0} \right\} \quad 7$$

The expression presented in Equation 8 can be used to evaluate current density (i) (Tafel equation) (Andreadris and Tsiakaras, 2006);

$$i = \{i_{0,\text{an}} \exp [\alpha_a \frac{nF}{RT} (E^{\circ} - E_{\text{eq}})] - i_{0,\text{cat}} \exp [\alpha_c \frac{nF}{RT} (E^{\circ} - E_{\text{eq}})] \} \quad 8$$

where i_0 represent exchange current density, $\alpha_{a,\text{anode}}$ represent the anodic transfer coefficient, $\alpha_{a,\text{cathode}}$ represent cathodic transfer coefficient

However, the exchange current density (i) is correlated as:

$$i_o = i_o^{\text{ref}} \square_o^{\text{eff}} \left(\frac{C_i}{C_i^{\text{ref}}} \right) \square \exp \left\{ \frac{-E}{RT} \left(1 - \frac{T}{T^{\text{ref}}} \right) \right\} \quad 9$$

i_o^{ref} = reference exchange current density, \square_o^{eff} = effective surface area, C_i = approximated surface concentration of the agglomerate, C_i^{ref} = reference reactant concentration, \square = reaction order, T^{ref} = reference temperature, E is the activation energy.

In a similar the manner, the concentration loss or potential (V_{conc}) as shown in Equation 6 can be evaluated using the relationship shown in Equation 10(Barbir, 2005)

$$V_{\text{conc}} = \frac{RT}{nF} \ln [1 - i/J_L] \quad 10$$

Assabumrungrat et al (2005) in their work suggested that ohmic loss can be evaluated from the relationship shown in Equation 11

$$V_{\text{ohmic}} = (\gamma \exp \left[\beta \left(\frac{1}{T_{\text{op}}} - \frac{1}{T_{\text{ref}}} \right) \right]) i_{\text{cat}} \quad 11$$

Recall from Equation 4 i.e. $V_{\text{cell}} = V_{\text{rev}} - V_{\text{irrev}}$, substitute Equations 5, 7, 10 and 11 into this equation (Equation 4) to obtain;

$$V_{\text{cell}} = E^0 - \frac{RT}{nF} \ln \left[\left(\frac{i}{i_{\text{oa}}} \right) \frac{1}{\alpha_{\text{oa}}} \left(\frac{1}{i_{\text{oc}}} \right) \frac{1}{\alpha_{\text{oc}}} \times \left(\frac{J_L - i}{J_L} \right) \times \left(\frac{P_{\text{H}_2\text{O}}^3 \times P_{\text{CO}_2}^2}{P_{\text{O}_2}^3} \right) - i \gamma \exp \left[\beta \left(\frac{1}{T_{\text{op}}} - \frac{1}{T_{\text{ref}}} \right) \right] \right] \quad 12$$

Equation 12 is the developed predictive mathematical model for the prediction of output voltage of DEFC. Efficiency of the DEFC defined as the ratio of the predictive cell output voltage (V_{cell}) and the standard cell potential E^0 as shown in Equation 13

$$\eta_{\text{cell}} = \frac{V_{\text{cell}}}{E^0} \times 100 \quad 13$$

Since the reactions that produce the energy in fuel cell is incomplete, there is therefore the need to consider fuel utilization while computing the fuel cell efficiency. Abdulkareem et al (2010) define fuel cell utilization as;

$$\delta_f = \frac{\text{Mass of fuel (methanol) reacted in the cell}}{\text{Mass of fuel (methanol) unreacted in the cell}} \quad 14$$

Substitute Equation 14 into Equation 13 to obtain;

$$\eta_{cell} = \delta_f \frac{V_{cell}}{E^0} \times 100 \quad 15$$

2.2 Mass Balance for the DEFC

The mass flow rates of the reactants i.e. ethanol and oxygen (Figure 1a) can be evaluated based on Faraday's law as shown in Equation 16 and 17 respectively.

[Figure 1a Here]

$$m_{C_2H_5OH, in} = m_{C_2H_5OH, react} + m_{C_2H_5OH, out} \quad 16$$

$$m_{O_2, in} = m_{O_2, react} + m_{O_2, out} \quad 17$$

The rate of consumption of ethanol in the cell is given by Yilanci et al., (2008) as:

$$m_{C_2H_5OH, react} = \zeta_A M_{C_2H_5OH} \frac{JA_{cell}}{6F} \times 10^{-3} \quad 18$$

Where ζ_A = anode stoichiometry, $M_{C_2H_5OH}$ = molecular weight of ethanol, J = current density (A/cm^2), A_{cell} = effective surface area of the cell (m^2), F = Faraday's constant (C/mol).

Ozturk, 2008 suggested that the rate of oxygen consumption in the cell can be evaluated from the relationship shown in Equation 19;

$$m_{O_2, react} = \zeta_C M_{O_2} \frac{JA_{cell}}{6F} \times 10^{-3} \quad 19$$

Where ζ_C = cathode stoichiometry and M_{O_2} = molecular weight of oxygen.

Production of water and CO_2 in the DEFC can be evaluated using relationship shown in Equations 20 and 21 respectively:

$$m_{\text{H}_2\text{O},\text{out}} = M_{\text{H}_2\text{O}} \frac{J_{\text{Acell}}}{6F} \times 10^{-3} \quad 20$$

$$m_{\text{CO}_2,\text{out}} = M_{\text{O}_2} \frac{J_{\text{Acell}}}{6F} \times 10^{-3} \quad 21$$

Similarly the rate of ethanol and oxygen out of the system can be evaluated from the relationship shown in Equations 22 and 23 respectively;

$$m_{\text{C}_2\text{H}_5\text{OH},\text{out}} = m_{\text{C}_2\text{H}_5\text{OH},\text{in}} - m_{\text{C}_2\text{H}_5\text{OH},\text{react}} \quad 22$$

$$m_{\text{O}_2,\text{out}} = m_{\text{O}_2,\text{in}} - m_{\text{O}_2,\text{react}} \quad 23$$

$$\text{hence, } m_{\text{C}_2\text{H}_5\text{OH},\text{out}} = m_{\text{C}_2\text{H}_5\text{OH},\text{in}} - \zeta_A M_{\text{C}_2\text{H}_5\text{OH}} \frac{J_{\text{Acell}}}{6F} \times 10^{-3} \quad 24$$

$$m_{\text{O}_2,\text{out}} = m_{\text{O}_2,\text{in}} - \zeta_C M_{\text{O}_2} \frac{J_{\text{Acell}}}{6F} \times 10^{-3} \quad 25$$

2.3 Energy Analysis of Direct Ethanol fuel cell

From Figure 1b, energy balance of the system is;

[FIGURE 1b HERE]

$$Q_{\text{input}} - Q_{\text{output}} - Q_{\text{acc}} = 0 \quad 26$$

Where Q_{input} and Q_{output} are the total heat input and output respectively, and Q_{acc} is the heat accumulation which is the net heat generated by physical and chemical processes within the cell. Replacing Q_{acc} with Q_{net} in Equation 26 and re-arrange to obtain;

$$Q_{\text{net}} = Q_{\text{input}} - Q_{\text{output}} \quad 27$$

From Figure 2, the heat input into the system is

$$Q_{\text{input}} = Q_{\text{C}_2\text{H}_5\text{OH},\text{in}} + Q_{\text{O}_2,\text{in}} \quad 28$$

Where $Q_{\text{C}_2\text{H}_5\text{OH},\text{in}}$ and $Q_{\text{O}_2,\text{in}}$ are the heats from the feed of the reactant.

In a similar manner, the total heat output from the system is:

$$Q_{\text{output}} = Q_{\text{C}_2\text{H}_5\text{OH},\text{out}} + Q_{\text{O}_2,\text{out}} + Q_{\text{H}_2\text{O}} + Q_{\text{CO}_2} + Q_{\text{rxn}} + Q_E + Q_{\text{loss}} \quad 29$$

Equation 27 can be rearranged and evaluated in terms of enthalpies to obtain;

$$Q_{\text{net}} = \Delta H_{\text{C}_2\text{H}_5\text{OH},\text{in}} + \Delta H_{\text{O}_2,\text{in}} - \Delta H_{\text{C}_2\text{H}_5\text{OH},\text{out}} - \Delta H_{\text{O}_2,\text{out}} - \Delta H_{\text{H}_2\text{O}} - \Delta H_{\text{CO}_2} - i \left(n - \frac{T\Delta S}{nF} \right) - E_{\text{cell}} \times IT - h_{\text{nc}} A_{\text{FC}} (T_{\text{FC}} - T_0) - m_{\text{coolant}} C_{p,\text{air}} (T_{\text{coolant},\text{out}} - T_0) - \sigma A_{\text{FC}} (T_{\text{FC}}^4 - T_0^4) \quad 30$$

Equation 30 is the model equation representing the net heat generated by the DEFC.

3. Results and discussion

This study is focus on the development of predictive model for performance of DEFC. Simulated results obtained on the effects of various parameters such as temperature, pressure and fuel and oxidant concentration on the output voltage, efficiency and heat generated are hereby presented. Effects of temperature on the performance of DEFC were simulated with computer and the results obtained are presented (Figure 2). It can be observe from Figure 2 that increase in current density resulted into decrease in the cell output voltage. For instance, at operating temperature of 303⁰K the cell output voltage decreased from 1.075 V to 1.0647 V when the current density increase from 0 to 45 mA/cm². Results also indicate that voltage output of the cell decrease with increase in temperature. When the system was simulated at operating temperature of 313⁰K, the cell output voltage ranges from 1.0729V to 1.0587V when the current density increases from 0 to 45mA/cm². Operating the cell at the same current density of 0 to 45mA/cm² with operating temperature of 333⁰K the cell output voltage obtained was 1.07068 V to 1.0517V. The observed decrease in the cell voltage as the operating temperature was increased is due to ohmic over potential in the cell, which is described as the barrier to electron and ions flow through the electrode and the cell interconnectivity (Abdulkareem et al, 2010)

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3 **[FIGURE 2 HERE]**
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6 Presented in Figure 3 are the simulated effects of ethanol concentration on the DEFC
7 performance. Simulated results show that when the ethanol concentration increased from
8 0.125M to 1M, the cell output voltage obtained increased from 1.07528 V to 1.07808 V.
9 Results also indicate that simulated output voltage decreases with increase in current density.
10 The observed increase in the cell voltage as the ethanol concentration was increased is due to
11 the participation of more ethanol in the electrochemical reaction, as current density is
12 increased more ethanol oxidation reaction that occurs at the anode, leading to reduction in the
13 ethanol concentration between the anode and cathode respectively. Effects of varying the
14 oxygen concentration on the performance of the cell were simulated and the results obtained
15 are presented in Figure 4. It can be observed from the results presented that varying the
16 concentration of oxygen positively affects the performance of the cell.
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33 **[FIGURES 3 & 4 HERE]**
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35 Also simulated in this study are the effects of cathode and anode pressure on the voltage
36 output of DEFC were also simulated. The cathode operating pressure was varies from 016 to
37 0.46 bar, results obtained revealed that the cell output voltage increase with increase in
38 operating cathode pressure. Presented in Figure 5 are the simulated results of the predictive
39 model of cell voltage against current density behaviour at four different anode pressures.
40 Results obtained on the effects of anode pressure on the performance of cell are similar to
41 that of cathode. This pattern of results can be attributed to the fact increase in cathode and
42 pressure resulted into increase in volume of oxygen and ethanol available for the
43 electrochemical reaction, which in turn reduces ethanol crossover.
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55 **[FIGURES 5 HERE]**
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3 This study also attempts to simulate the effect of temperature on the direct methanol fuel cell
4 efficiency by varying the operating temperature between 303°K to 343°K with step length of
5 100°K. Results obtained indicate that operating temperature negatively affect the efficiency
6 of the cell. At operating temperature of 303°K, the cell efficiency obtained was 93.91%, when
7 the operating increase to 343°K, the cell efficiency reduces to 92.99%. The observed
8 reduction in the cell efficiency with increase in operating temperature can be attributing to the
9 destruction of the membrane matrix at high operating temperature which leads to the fuel
10 (ethanol) crossover that affects the performance of the cell negatively. Heat is a by-product of
11 the electrochemical reaction that produces energy in fuel cell technologies (Abdulkareem et
12 al, 2013). However, care must be taken to control the heat generated, since excessive heat in
13 the system can dehydrate the proton exchange membrane component of the cell, which will
14 result into poor performance of the cell. It was on this basis that this study also attempts to
15 develop a predictive mathematical model for the heat generation by the cell during operation
16 (Equation 31), the developed model was also simulated and the results obtained are presented
17 in Figure 6. The results obtained on the influence of temperature on the net heat generation
18 by the proton exchange membrane fuel cell fuelled with ethanol as presented in Figure 9
19 indicate heat generated is directly proportional to the operating temperature. This implies that
20 the higher the operating temperature the higher the heat generated by the cell. This pattern of
21 results can be attributed to the fact at higher temperature the rate of electrochemical reaction
22 in the cell will be high which will result in high generation of heat of reaction.
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47 **[FIGURES 6 HERE]**
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49 **4. Conclusion**

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51 This study focus on the development of a predictive mathematical model for the performance,
52 efficiency and heat generation by the DEFC, for the purpose of study the influence of
53 temperature, pressure and fuel and oxidant concentration on the cell performance. A Java
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3 computer program was use for the simulation of the predicted model while considering the
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5 various parameters. It can be inferred from the simulation results obtained that increase in
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7 temperature led to reduction in the cell output voltage as well as its efficiency, however the
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9 heat generated by the fuel cell increases. Simulated results also reveal that the operating
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11 pressure of both anode and cathode ethanol positively affects the voltage output of the cell.
12
13 Increase in concentration of both ethanol and oxygen also increase the voltage output of the
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15 cell. Hence the developed model can be use as a tool to theoretically predict the fuel cell
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17 performance.
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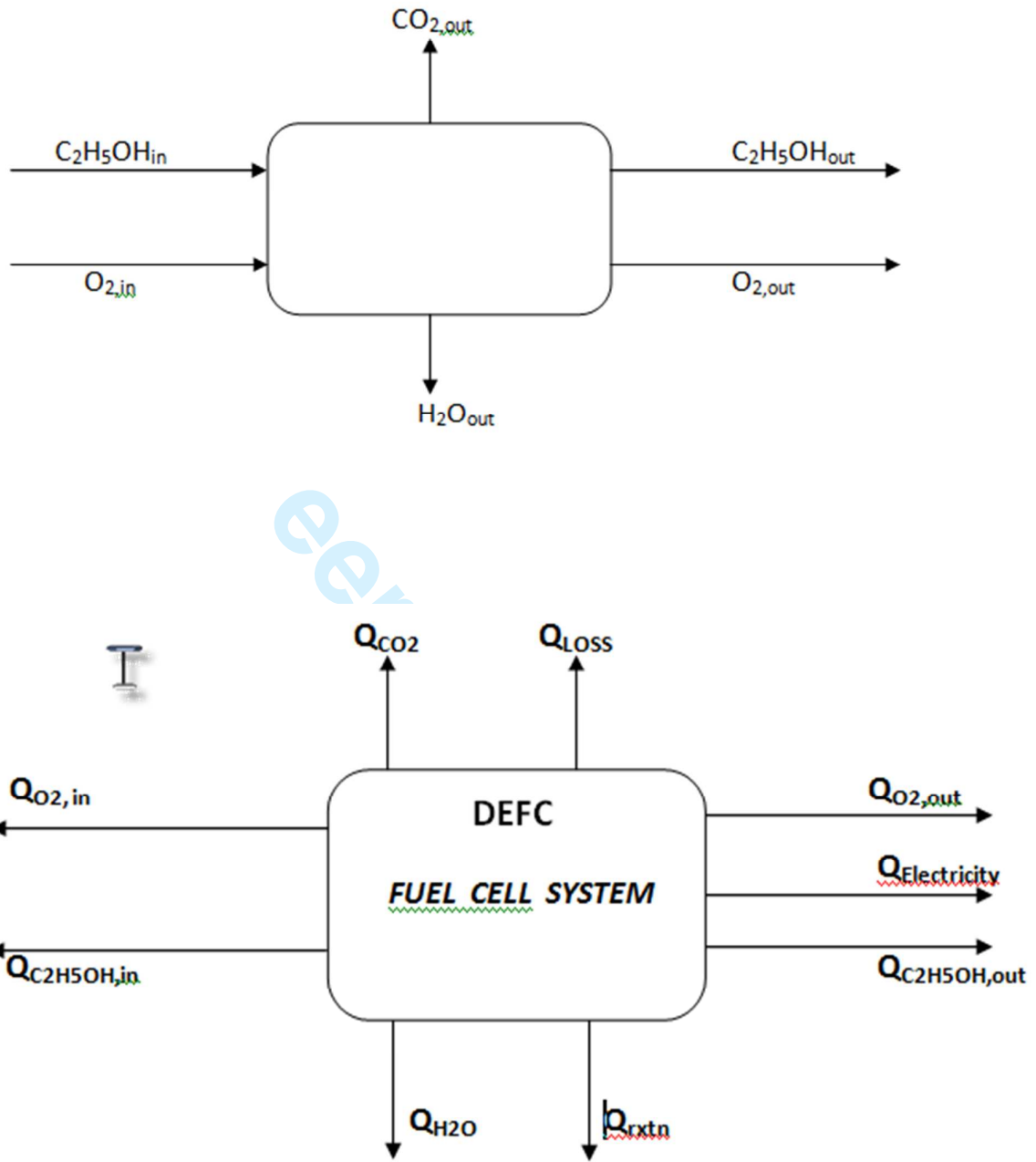


Figure 1: (a) Schematic Mass Balance for the DEFC (b) Energy balance in direct methanol fuel cell

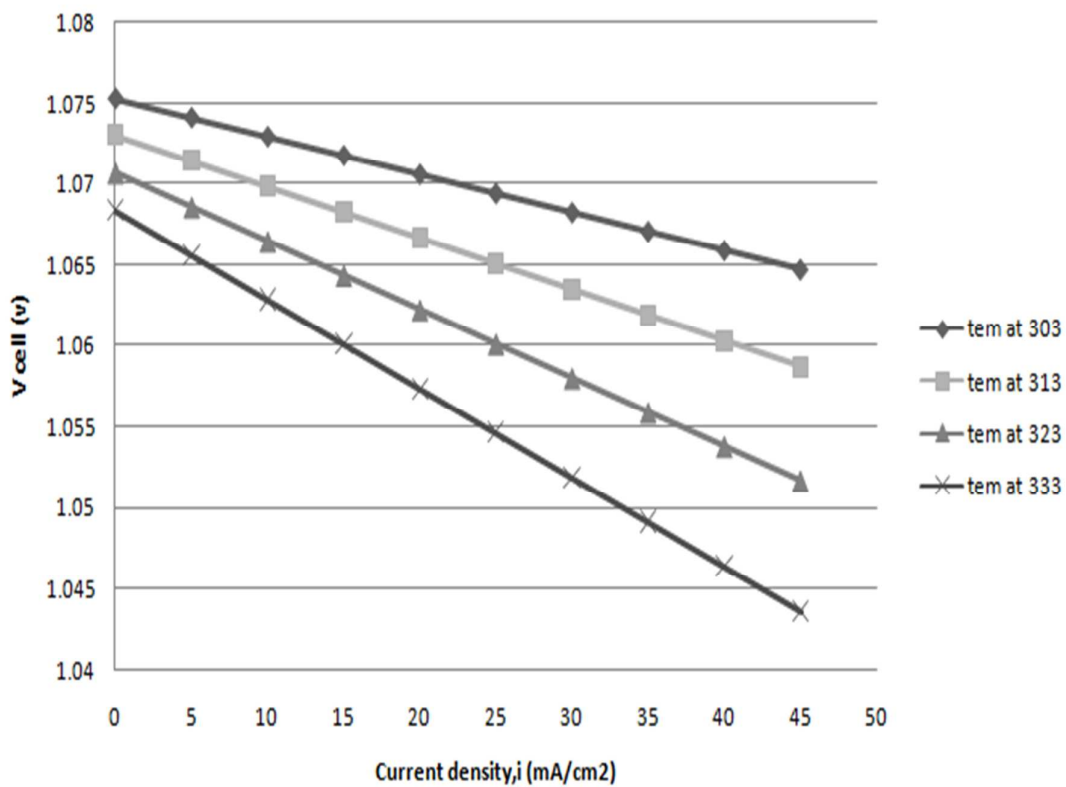


Figure 2: Simulated results on the influence of temperature on the output voltage of DEFC.

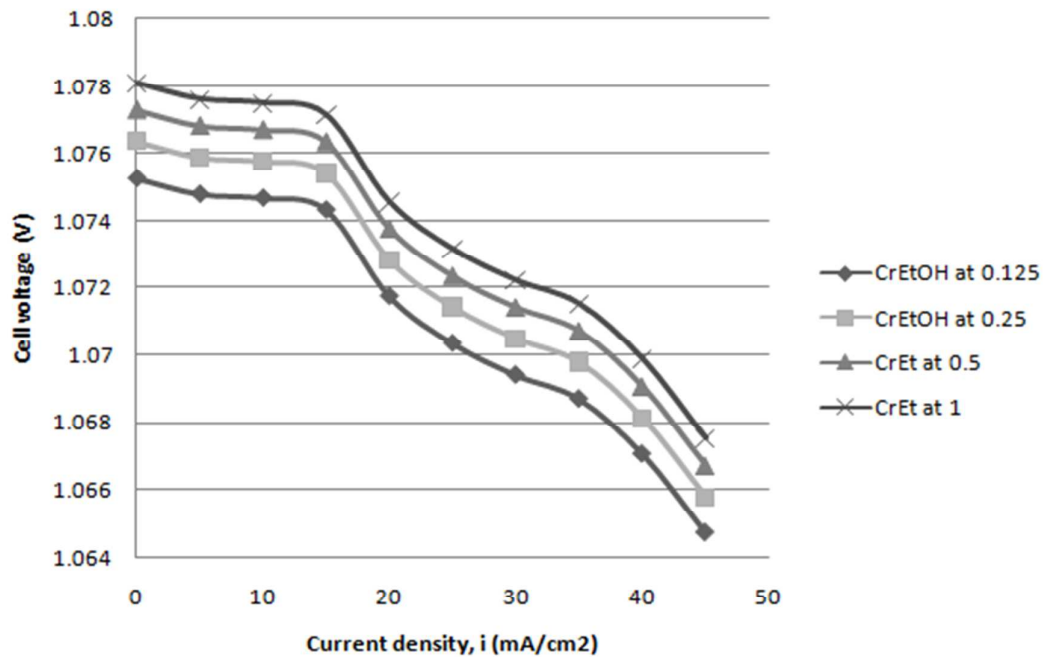


Figure 3: Simulated result on the influence of ethanol concentration on the voltage output of DEFC.

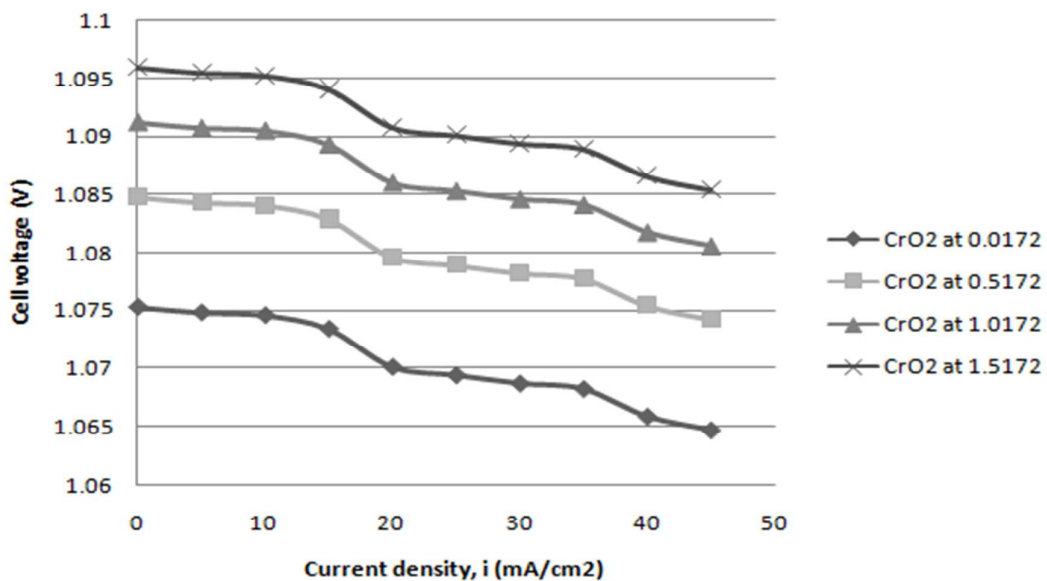


Figure 4: Simulated results on the influence of oxygen concentration on the voltage output of DEFC.

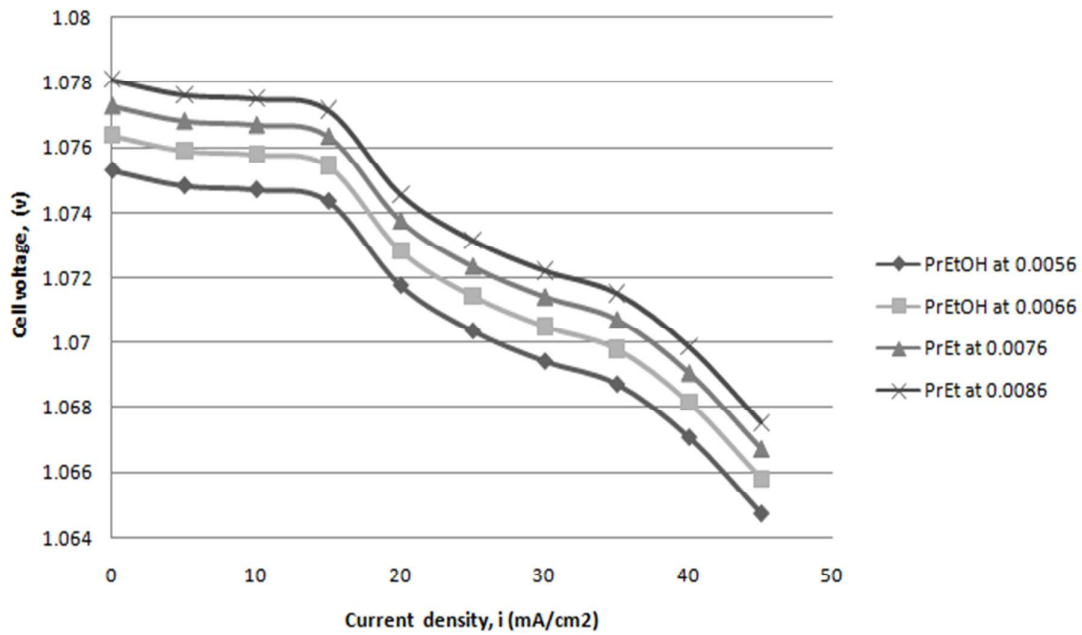


Figure 5: Simulated influence of anode pressure on the output voltage of DEFC.

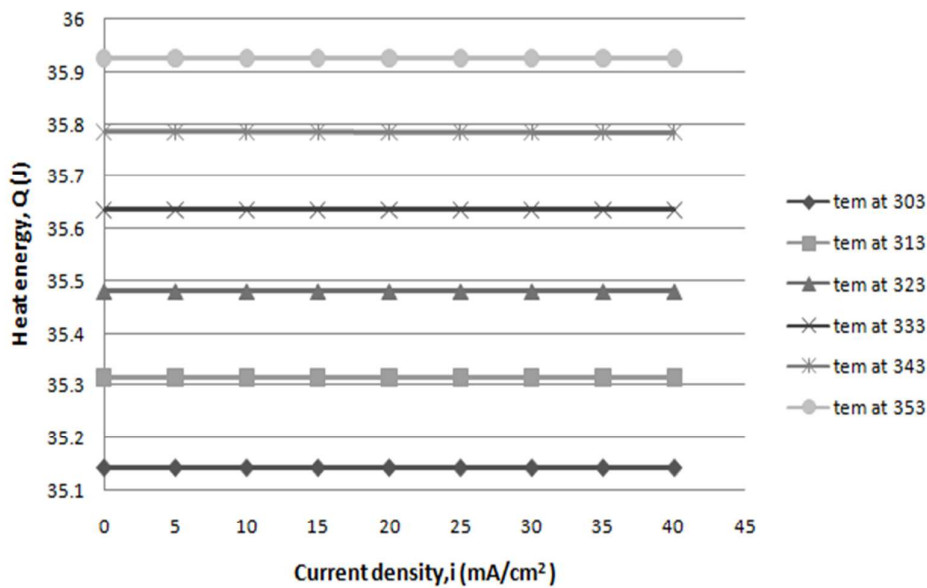


Figure 6: Simulated influence of temperature on the heat generated by DEFC.